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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The borane framework expansion reaction by the use of $B_2H_4 \cdot 2P(CH_3)_3$ which was discovered during the previous ARO contract research period, was developed to be a more general type of reaction. The B_2H_4 adducts containing Lewis bases other than $P(CH_3)_3$ were tested for the expansion reaction or used to interpret formations of higher borane compounds. The formation of $B_5H_{11} \cdot PH_2^-$ from $B_4H_8 \cdot PH_3$ and $NaBH_4$ is cited as a case of new in-situ BH_3 addition to borane species. A further insight into the formation of the B_2H_4 adducts from the B_3H_7 adduct was obtained. The treatment of $B_3H_7 \cdot S(CH_3)_2$ with $N(CH_3)_3$ in CH_2Cl_2 at $-80^\circ C$ resulted in the immediate formation of $B_2H_4 \cdot 2N(CH_3)_3$, suggesting that the same type of reaction might be advantageously used to prepare thermally unstable B_2H_4 adducts. (continue on reverse) | | | |
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Block 18, continued:

$B_3H_7 \cdot 3P(CH_3)_3^+$, formation of; $B_2H_6 \cdot P(CH_3)_3^+$, formation of; $B_5H_8 \cdot P(CH_3)_3^+$, reaction with $P(CH_3)_3$; $B_2H_4 \cdot 2N(CH_3)_3$, formation of; B_3H_7 adducts, cleavage of; $B_2H_4 \cdot 2N(CH_3)_3$; $B_2H_4 \cdot N(CH_3)_3$; $P(CH_3)_3$; $B_2H_4 \cdot 2S(CH_3)_2$; $B_4H_8 \cdot S(CH_3)_2$; $B_4H_8 \cdot P(CH_3)_3$; Base-influenced fluxionality; $B_3H_7 \cdot 2P(CH_3)_3$; $B_4H_8 \cdot 2N(CH_3)_3$; $B_4H_7 \cdot 3P(CH_3)_3^+$; $B_5H_7 \cdot P(CH_3)_3$; $B_3H_6 \cdot 2S(CH_3)_2^+$; $B_3H_7 \cdot S(CH_3)_2$.

Block 19, continued:

When $B_4H_8 \cdot S(CH_3)_2$ was dissolved in $S(CH_3)_2$, the basal three boron atoms of the B_4H_8 fragment became equivalent on the NMR time scale. This phenomenon of solvent-promoted fluxionality was interpreted in terms of a weak interaction between the B_4H_8 adduct and the solvent base. The same was observed for $B_4H_8 \cdot P(CH_3)_3$ in $S(CH_3)_2$. In contrast, the fluxional motion of $B_4H_8 \cdot 2P(CH_3)_3$ is slowed down by the presence of free base in the solution.

The number of homolog series of polyboron complex cations has now been increased to five. Similarities and differences in reactivities between these cationic species and the corresponding isoelectronic, neutral borane species have been encountered. Preparation of polyboron complex cations containing SR_2 was intended. The $B_3H_6 \cdot 2S(CH_3)_2^+$ cation was tentatively identified.

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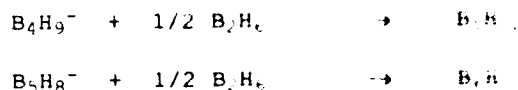
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I. Background and Objectives

Stock's early syntheses of boron hydrides involved the reaction of a rather poorly defined magnesium boride with aqueous phosphoric acid.¹ Miserable yields of a hydride mixture containing large percentages of higher hydrides were obtained. All subsequent procedures, based largely on the work of Schlesinger, Brown, Burg, and their co-workers^{2,3} as well as some commercial programs,⁴ gave B_2H_6 as the sole initial product. Higher boranes (particularly those needed for the synthesis of carboranes) are currently made from diborane by thermolysis. Through proper selection of reaction conditions and equipment B_4H_{10} , B_5H_9 , B_6H_{10} , or $B_{10}H_{14}$ can be prepared in fair to good yields,⁵ but the processes are very difficult and expensive commercial operations. Three other rather generalized processes for converting B_2H_6 to higher hydrides have been of interest in the past decade. The first of these⁶ builds on earlier work of Hough, Marshall, Hunt, Hefferan, Adams, and Makhlouf of Callery Chemical Company. The process involves the pyrolysis of $[NR_4]BH_4$ to yield $[NR_4]_2B_{10}H_{10}$. This is followed by the opening of the $B_{10}H_{10}^{2-}$ cage with HCl in liquid $(C_2H_5)_2S$ to give $B_{10}H_{12} \cdot 2S(C_2H_5)_2$. From the latter diethyl sulfide adduct, carboranes can be obtained. Yields are marginal.

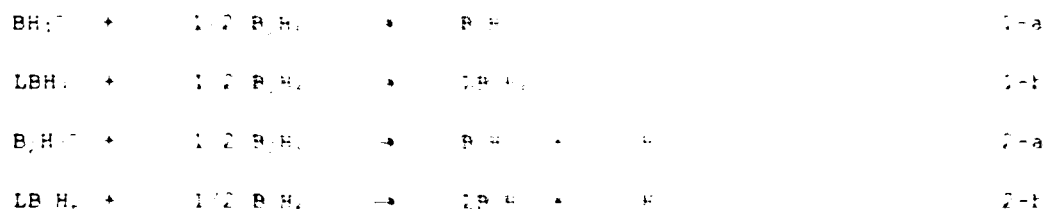
A second process involves the reaction of $NaBH_4$ with B_2H_6 . Following the early work of Hough and Edwards⁸ on the reactions of B_2H_6 with sodium amalgam to give $NaBH_4$ and NaB_3H_8 .⁹ Muetterties¹⁰ carried the process further and obtained $NaB_{11}H_{14}$ from $NaBH_4$ and B_2H_6 under different conditions. This general process has been developed beautifully in a fundamental sense by Shore and his students who have been able to build up large borane anions in a stepwise fashion by adding a borane group (Lewis acid) to a B-B bond in selected boron hydride anions.¹¹ Reactions such as those shown here were carried out:



Addition of a proton to the anion generated a neutral n-ane (n=4,5,6) boron more than the starting material. In a few cases n was less. A related process was developed in recent years by Jones and co-workers at the University of California, San Diego.

Shore and his co-workers further developed a systematic synthesis of B_2H_6 , B_4H_{10} , B_5H_{11} , and B_6H_{10} which involve the use of a catalyst and a Lewis acid BX_3 , and the resulting neutral n-ane species reacts with B_2H_6 which is available from an other source. The yields are excellent, and this process is the most convenient laboratory method presently available for the preparation of higher boranes.

The last process of interest might be considered a modification of the foregoing reactions involving a catalyst and a Lewis acid. If the catalyst replaces a hydride of BH_3 with a general Lewis base, the molecule LBH_2 is formed, where L is a ligand such as CH_3 , NH_2 , or OH . This species, like BH_2^- , will also pick up B_2H_6 to give larger n-ane species. For example, the following reactions can be prepared:



This process has some literature precedent. Some years ago Muetterties reported that the reaction of $\text{Si(CH}_3)_3$ with B_2H_6 at 200°C gives $\text{B}_2\text{H}_6 \cdot \text{Si(CH}_3)_3$. Several other conversions of similar type have also been reported.

In 1962 Burgi reported that hexamethylenetetramine and several other Lewis bases act catalytically in the conversion of B_2H_6 to B_4H_{10} , B_5H_{11} , and

B_5H_{11} . In considering this process it is reasonable to postulate that B_5H_{11} reacts initially with a Lewis base to give an adduct of general form LB_xH_y which can then react with additional B_5H_{11} (or another base borane adduct in the system) to give boron framework expansion. The reaction between B_5H_{11} and Lewis bases was thus of considerable importance in delineating the path for the expansion of the boron framework. Earlier reports on the reaction of B_5H_{11} with bases such as NR_3 had described a confusing process from which no base-borane products could be characterized.¹⁵ Thus our initial work focussed on the reactions of B_5H_{11} with Lewis bases. Subsequent work involved a study of the reactions of the products obtained from the base reaction with borane units or other boron sources. The goal of the study was an expansion of the boron framework.

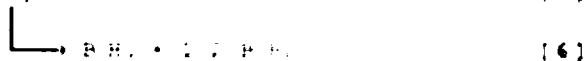
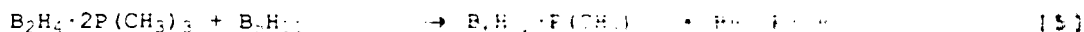
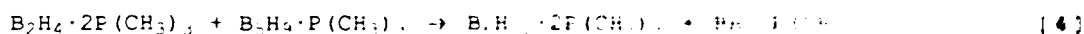
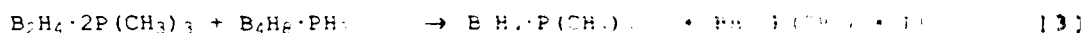
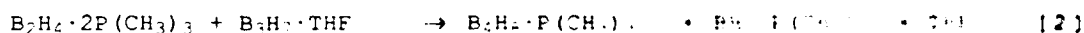
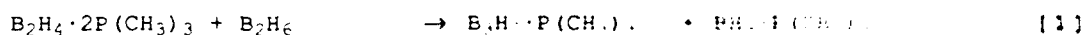
A brief summary of the results of our work performed under the sponsorship of the Army Research Office through DAAG29-76-G-0120, DAAG29-79-C-0129 and DAAG29-81-K-0101 was described in a paper entitled "Chemistry of Lower Boranes Involving Trimethylphosphine"¹⁶, which is attached to this report as Reprint #7. In short, during these earlier contract research periods, the strongly basic nature of $P(CH_3)_3$ was exploited to establish a number of definable reactions of lower boranes, which could then be used as guides for the studies of related complex reactions. Thus, at the beginning of this reporting period, we were ready to direct our effort to the study of borane reaction systems involving weaker Lewis bases.

II. Summary of the Results

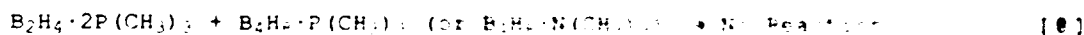
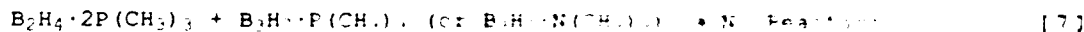
A. Borane Framework Expansion Reactions

1. Use of the B₂H₄ Adducts

Background. During the earlier ARO contract research periods, B₂H₄·2P(CH₃)₃ was found to serve as a borane framework expansion reagent. When B₂H₄·2P(CH₃)₃ was mixed with certain borane compounds, it split into BH₃·P(CH₃)₃ and ":BH·P(CH₃)₃", and the latter was added to the borane substrate to give a product containing an increased number of boron atoms. Examples are



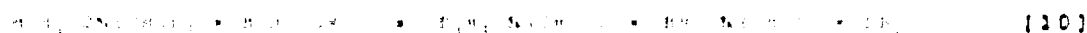
When the Lewis bases that are attached to the borane substrates are very strong the above expansion reaction will not proceed.



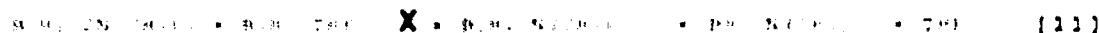
Apparently, the borane acidity of the substrate has to be sufficiently strong for the reaction to occur. When the strongly electron donating P(CH₃)₃ group is attached to the B₂H₄ or B₃H₈ fragment, the acidity of the borane is not strong enough to react with B₂H₄·2P(CH₃)₃ or B₃H₈·P(CH₃)₃, however, because of the stronger acidity of the B₂H₄ group, which is inherent in larger borane fragment,²¹ retains its acidity strong enough even in the presence of P(CH₃)₃ in the molecule, and reacts with B₂H₄·2P(CH₃)₃ to form B₃H₅·2P(CH₃)₃. It was

is further interest to test the same type of expansion reaction with the other BH_3 salts containing different Lewis bases (14, 15) and to interpret the results in terms of the above established framework expansion reaction.

$B_2H_6 \cdot 2N(CH_3)_3$ The more elusive trimethylamine adduct of B_2H_6 , $B_2H_6 \cdot 2N(CH_3)_3$, was successfully isolated and characterized during this study period. This BH_3 salt is described in the following expansion reaction:

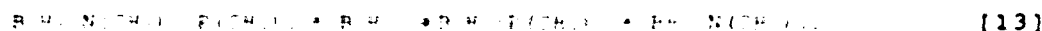


However, with $BH_3 \cdot THF$ and with BH_3 , the following salt is formed instead of the former similar salt described for $BH_3 \cdot THF$:



Instead, hydride adducts of trimethylamine, $BH_3 \cdot N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3 \cdot THF$ were formed in the reaction with $BH_3 \cdot THF$ and BH_3 , respectively. The nature of the reaction products are yet to be investigated.

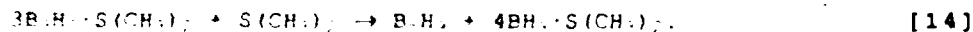
$B_2H_6 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ This newly prepared mixed-ligand adduct of B_2H_6 was tested for the reaction with BH_3 . The reaction observed was



In the product, the stronger base $P(CH_3)_3$ is attached to the expanded, stronger and BH_3 and the weaker base $N(CH_3)_3$ is combined with the weaker and BH_3 .

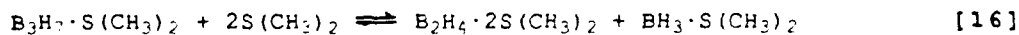
2. Formation of B_5H_9 from $B_3H_7 \cdot SR_2$ in SR_2 solutions.¹⁶

When $BH_3 \cdot S(CH_3)_2$ was dissolved in $S(CH_3)_2$ at room temperature, B_5H_9 formed slowly. The reaction was clean, and no hydrogen gas evolved. The appropriate equation for the reaction is



The series of ^{11}B NMR spectra (25.5 MHz, ^1H , room temperature) in Figure 1 shows the formation of B_5H_9 . Clearly, the relative intensity ratio between the low-field signal of B_5H_9 (at -13 ppm) and the $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ signal is 1:1 as Equation 14 demands, and no signals other than the reactants and products are seen.

Dimethyl thioether, $\text{S}(\text{CH}_3)_2$, is not a very strong base. The general trend of base strength toward boranes is $\text{P}(\text{CH}_3)_3 > \text{N}(\text{CH}_3)_3 > \text{S}(\text{CH}_3)_2 > \text{O}(\text{CH}_3)_2$. [15] Each member of this series is a base that is strong enough to react with B_2H_6 to give the corresponding adducts of B_2H_6 and BH_3 .²² However, although $\text{P}(\text{CH}_3)_3$ and $\text{N}(\text{CH}_3)_3$ are known to cleave the respective adducts of B_2H_6 to give the corresponding adducts of B_2H_6 ,²²⁻²³ dimethyl ether does not cleave $\text{B}_3\text{H}_7\cdot\text{O}(\text{CH}_3)_2$. Dimethyl thioether is situated in-between. It, therefore, is reasonable to postulate that the following equilibrium exists in a $\text{S}(\text{CH}_3)_2$ solution of $\text{B}_3\text{H}_7\cdot\text{S}(\text{CH}_3)_2$:



The $\text{B}_2\text{H}_4\cdot 2\text{S}(\text{CH}_3)_2$ thus formed would then react with $\text{B}_3\text{H}_7\cdot\text{S}(\text{CH}_3)_2$ in a manner similar to that shown in Section II.A.1 to give $\text{B}_4\text{H}_8\cdot\text{S}(\text{CH}_3)_2$ which would further react with $\text{B}_2\text{H}_4\cdot 2\text{S}(\text{CH}_3)_2$ to form " $\text{B}_5\text{H}_9\cdot\text{S}(\text{CH}_3)_2$ " (cf. Equations 2 and

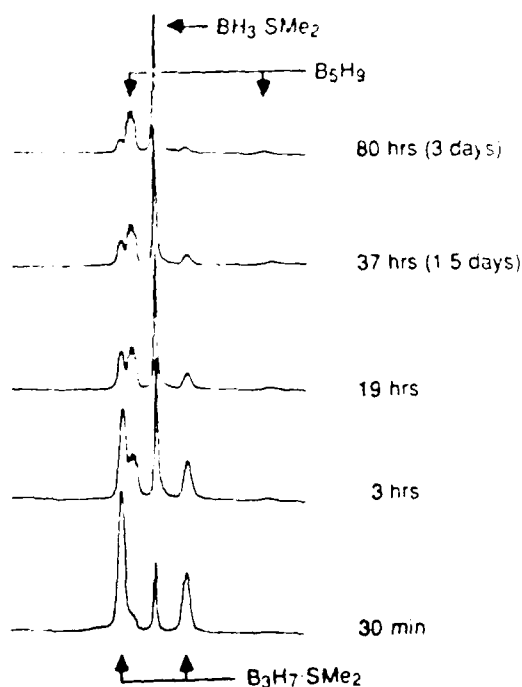
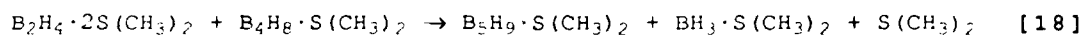
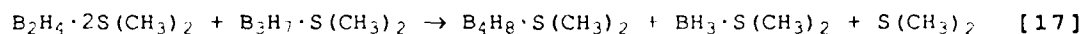


Figure 1. ^{11}B NMR spectra of $\text{B}_3\text{H}_7\cdot\text{S}(\text{CH}_3)_2$ in $\text{S}(\text{CH}_3)_2$: Slow formation of B_5H_9 .

10). The product " $B_5H_9 \cdot S(CH_3)_2$ " would readily eliminate $S(CH_3)_2$ to finally give B_5H_9 . See Equations 17-19.

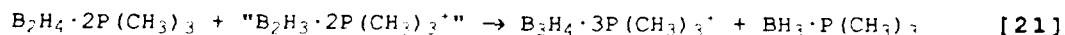
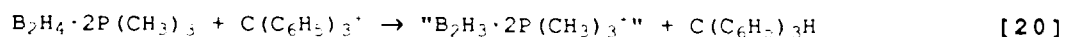


Equations 16 through 19 sum up to give Equation 14.

The above proposed mechanism for the formation of B_5H_9 suggests that, if $B_4H_8 \cdot S(CH_3)_2$ had been added to a $S(CH_3)_2$ solution of $B_3H_7 \cdot S(CH_3)_2$, the rate of the B_5H_9 formation would increase. Indeed, it was the case. When a $S(CH_3)_2$ solution containing $B_3H_7 \cdot S(CH_3)_2$ and $B_4H_8 \cdot S(CH_3)_2$ in a 1:1 molar ratio was prepared, the formation of B_5H_9 was complete in a few hours; $B_3H_7 \cdot S(CH_3)_2$ was consumed completely and a small portion of $B_4H_8 \cdot S(CH_3)_2$ remained in the solution. Thus the above interpretation, which is based on the $B_2H_4 \cdot 2P(CH_3)_3$ model, appears to be satisfactory.

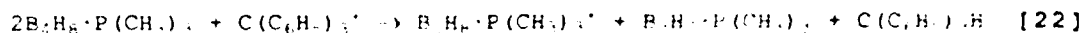
3. A More Generalized View of the Framework Expansion Reaction.

In the framework expansion reactions involving the B_2H_4 adducts, the substrate abstracts " $BH \cdot L$ " from $B_2H_4 \cdot 2L$ and $BH_3 \cdot L$ is eliminated. Therefore, the stability of $BH_3 \cdot L$ and the electrophilicity of the borane substrate are thought to be important factors to successfully drive the expansion reaction. In this sense, the formation of the $B_3H_4 \cdot 3P(CH_3)_3^+$ cation from $B_2H_4 \cdot 2P(CH_3)_3$ and the trityl cation²⁶ may be explained by the following scheme.

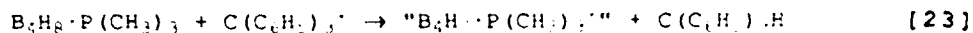


The intermediate " $B_2H_3 \cdot 2P(CH_3)_3^+$ " is a strong electrophile owing to its positive charge, and therefore reacts readily with $B_2H_4 \cdot 2P(CH_3)_3$, abstracting " $BH \cdot P(CH_3)_3$ " from $B_2H_4 \cdot 2P(CH_3)_3$ and liberating $BH_3 \cdot P(CH_3)_3$.

The frame work expansion scheme, which is discussed here, may further be extended to include a more general case. Consider the following reaction which was observed in this laboratory. (See attached Reprint #8)



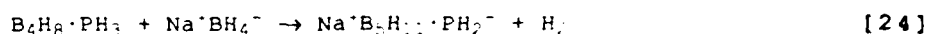
If the first step of the reaction is



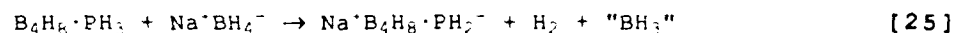
The electrophile " $B_4H_8 \cdot P(CH_3)_3$ " will abstract a ":BH" unit from $B_4H_8 \cdot P(CH_3)_3$ and liberate the stable triborane(7) adduct, $B_3H_7 \cdot P(CH_3)_3$. Further extension of this generalized view is obvious, and is a subject of further study.

4. In-Situ Addition of BH_3 to Borane Framework.

When $B_4H_8 \cdot PH_3$ was treated with $NaBH_4$ in tetrahydrofuran the following reaction occurred at $-40^\circ C$.¹⁹



The reaction (Equation 24) is thought to have proceeded in two steps:



It is known that $BH_3 \cdot PH_3$ and $B_3H_7 \cdot PH_3$ react with $NaBH_4$ to give $Na^+BH_3 \cdot PH_2 \cdot BH_3^-$ and $Na^+B_3H_7 \cdot PH_2 \cdot BH_3^-$, respectively.^{27,28} In these two reactions, the first step is the deprotonation of the phosphine hydrogen to form $BH_3 \cdot PH_2^-$ and $B_3H_7 \cdot PH_2^-$, respectively, in manners similar to that shown in Equation 25. Then, the generated BH_3 (or B_2H_6) adds to the phosphorus atoms of these anions to give the $BH_3 \cdot PH_2 \cdot BH_3^-$ and $B_3H_7 \cdot PH_2 \cdot BH_3^-$ anions. The $B_4H_8 \cdot PH_2^-$ anion which is produced in Equation 25, however, does not combine with BH_3 at the phosphorus atom to form $B_4H_8 \cdot PH_2 \cdot BH_3^-$. This is because, due to the enhanced borane acidity of the B_4H_8 fragment relative to those of B_3H_7 and BH_3 , the lone pair electrons on the phosphorus atom in $B_4H_8 \cdot PH_2^-$ is not readily available for the

P-BH₃ bond formation. Instead, the generated BH₃ adds to the B₄H₈ moiety to give the B₅H₉⁻·PH₃⁻ anion. Shore reported²¹ the addition of BH₃ to B₄H₉⁻:



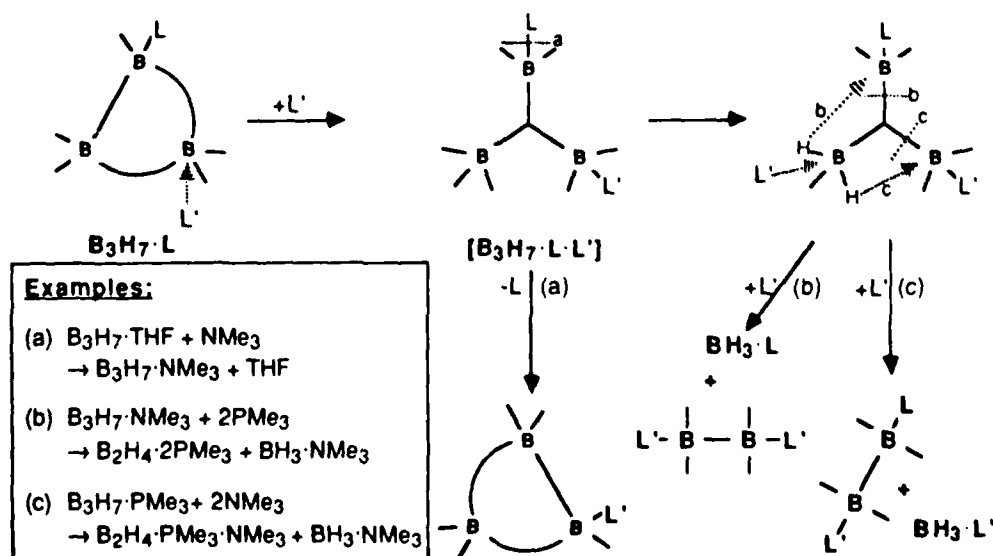
Thus, the B₅H₉⁻·PH₃⁻ anion behaves like the B₅H₉⁻ anion. (Note that these two anions are isoelectronic to each other.)

The in-situ addition of BH₃ of this type may further be developed to include higher borane compounds, and may conveniently be used to convert smaller borane fragments to larger structures by the use of NaBH₄ in place of B₂H₆.

B. Formation of B₂H₄ Adducts from B₃H₇ Adducts

Background. Reactions of triborane(7) adducts (B₃H₇·L) with Lewis bases (L') can proceed in two different ways: (1) displacement of the ligand base, and (2) cleavage of the triborane framework into the adducts of B₂H₄ and BH₃. A mechanism was proposed for these reactions by Ritter and co-workers,²⁹ and by Paine and Parry.³⁰ Central to the mechanism is the formation of an intermediate B₃H₇·L·L' which subsequently proceeds in the two different pathways depending upon the nature of the Lewis bases involved. See Scheme 1.

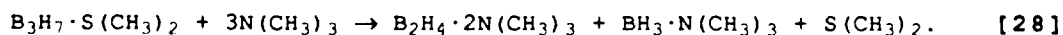
Scheme 1



In view of the potential use of the B_2H_4 adducts as reagents for borane framework expansion, and since the B_3H_7 adducts are a convenient source of the B_2H_4 adduct preparation, it was of interest to investigate in more details the cleavage pattern of B_3H_7 adducts. This study was rewarding in that not only the formerly elusive $B_2H_4 \cdot 2N(CH_3)_3$ was isolated but also the preparation of a mixed-ligand adduct $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ ²³ and an efficient way of preparing amine adducts of B_2H_4 ²⁴ could be formulated as a result of the study.

Preparation of $B_2H_4 \cdot 2N(CH_3)_3$ and $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$. The details of these studies are described in two published papers^{22,23}, reprints of which are attached to this report. (See Reprint #3 and #9). The preparation of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ by the reaction of $B_3H_7 \cdot P(CH_3)_3$ with $N(CH_3)_3$ is superior to that involves the displacement of $N(CH_3)_3$ from $B_2H_4 \cdot 2N(CH_3)_3$ by $P(CH_3)_3$; the reaction is faster and the product is purer. In addition, the quantitative formation of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ has provided an important insight into the cleavage pattern of triborane adducts, from which the facile preparation of $B_2H_4 \cdot 2N(CH_3)_3$ was developed.

Formation of $B_2H_4 \cdot 2N(CH_3)_3$ from $B_3H_7 \cdot S(CH_3)_2$.²⁴ Treatment of $B_3H_7 \cdot S(CH_3)_2$ with excess $N(CH_3)_3$ at $-80^\circ C$ in dichloromethane results in the immediate formation of $B_2H_4 \cdot 2N(CH_3)_3$. The appropriate equation for the reaction is



The reaction of $B_3H_7 \cdot N(CH_3)_3$ with $N(CH_3)_3$ to form $B_2H_4 \cdot 2N(CH_3)_3$ proceeds slowly at $0^\circ C$.²⁸ Therefore, the formation of $B_2H_4 \cdot 2N(CH_3)_3$ in Equation 28 is not the result of initial displacement of $S(CH_3)_2$ by $N(CH_3)_3$ to form $B_3H_7 \cdot N(CH_3)_3$ followed by the cleavage of the B_3H_7 fragment. Instead, the intermediate $B_3H_7 \cdot S(CH_3)_2 \cdot N(CH_3)_3$ must have undergone a rapid BH_3 -adduct

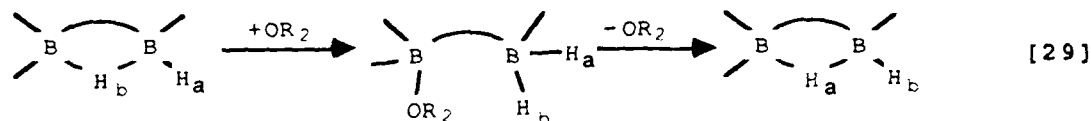
References on pages 19-20

$[\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2 \text{ or } \text{BH}_3 \cdot \text{N}(\text{CH}_3)_3]$ elimination upon interaction with $\text{N}(\text{CH}_3)_3$ according to pathway b or c in Scheme 1.

This low temperature formation of $\text{B}_2\text{H}_4 \cdot 2\text{N}(\text{CH}_3)_3$ should have a wider application to the syntheses of certain B_2H_4 adducts, where the use of higher temperatures is prohibited because of the thermal instability of the adducts.

C. Base-Influenced Fluxionality of B_4H_8 Adducts.²⁴

Background. In 1963, Gaines reported⁹ that the six hydrogen atoms of B_2H_6 became equivalent on the NMR time scale when B_2H_6 was dissolved in diglyme at room temperature. This phenomenon was explained by a weak interaction of B_2H_6 with the solvent ether to form an unstable intermediate, which upon reverting to B_2H_6 the terminal and bridge hydrogen atoms are interchanged.



Thus, the rapid H atom migration is induced in the diborane molecules when the co-existing base has an appropriate base strength relative to the strength of the B-H-B bridge bond.

This phenomenon of base-induced fluxionality should be a common occurrence among the lower boron hydride compounds, because most of them are "electron deficient" and are capable of interacting with Lewis bases to form more opened structures which can often undergo facile rearrangements. Elucidation of the interactions, in particular those with weaker bases, is of considerable interest to us; weak bases often play subtle but important roles in the transformation of borane compounds.

$\text{B}_4\text{H}_8 \cdot \text{SR}_2$ in SR_2 . Shown in Figure 2 are the ^{11}B NMR spectra (25.5 MHz, $\{^1\text{H}\})$ of $\text{B}_4\text{H}_8 \cdot \text{S}(\text{CH}_3)_2$ in two different solvents (CH_2Cl_2 and $\text{S}(\text{CH}_3)_2$) at two

different temperatures. Clearly, when $B_4H_8 \cdot S(CH_3)_2$ is dissolved in $S(CH_3)_2$ the signals of the $B_{2,4}$ and B_3 atoms coalesce at $+20^\circ C$. Similarly, the same coalescence was observed for $B_4H_8 \cdot S(C_2H_5)_2$ and $B_4H_8 \cdot THT$ (THT=tetrahydrothiophene) in $S(C_2H_5)_2$ and THT, respectively. The temperatures of coalescence paralleled with the base strength of the thioethers: $B_4H_8 \cdot S(CH_3)_2$; $+20^\circ C$, $B_4H_8 \cdot THT$; $+30^\circ C$, $B_4H_8 \cdot S(C_2H_5)_2$; $+45^\circ C$.

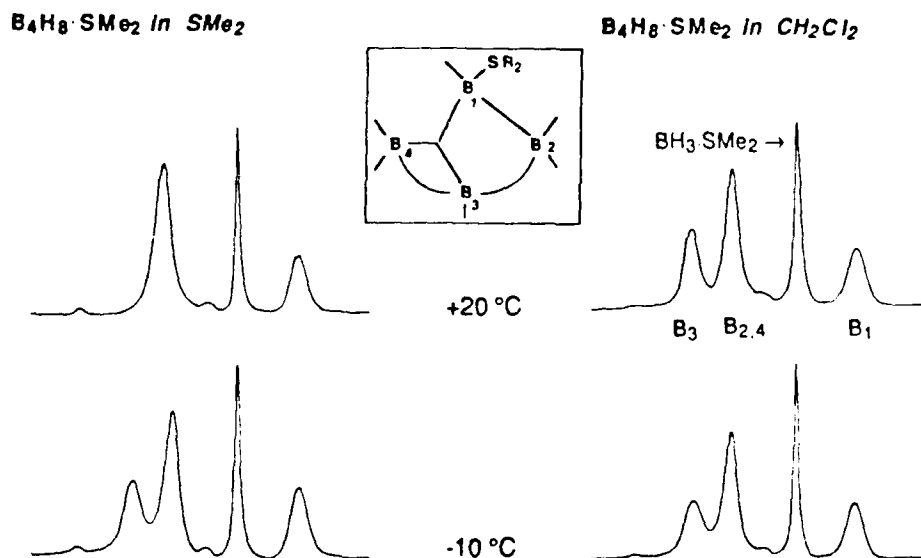
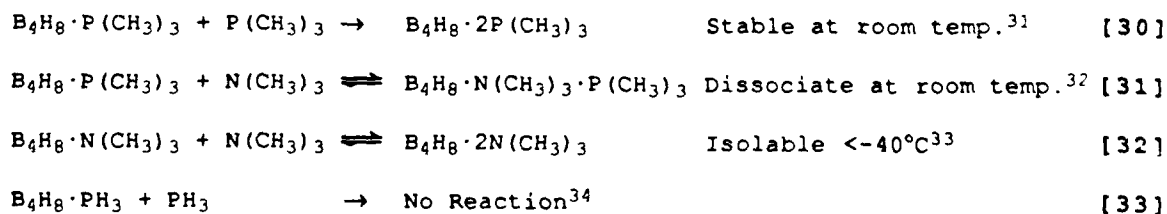


Figure 2. ^{11}B NMR spectra of $B_4H_8 \cdot S(CH_3)_2$: $S(CH_3)_2$ -induced fluxionality.

Many tetraborane(8) adducts, $B_4H_8 \cdot L$, are known to combine with bases to form bis(base) adducts of B_4H_8 . The stability of the bis(base) adducts depends upon the nature of the Lewis bases involved, and generally parallels with the strength of the base as indicated in the following examples.

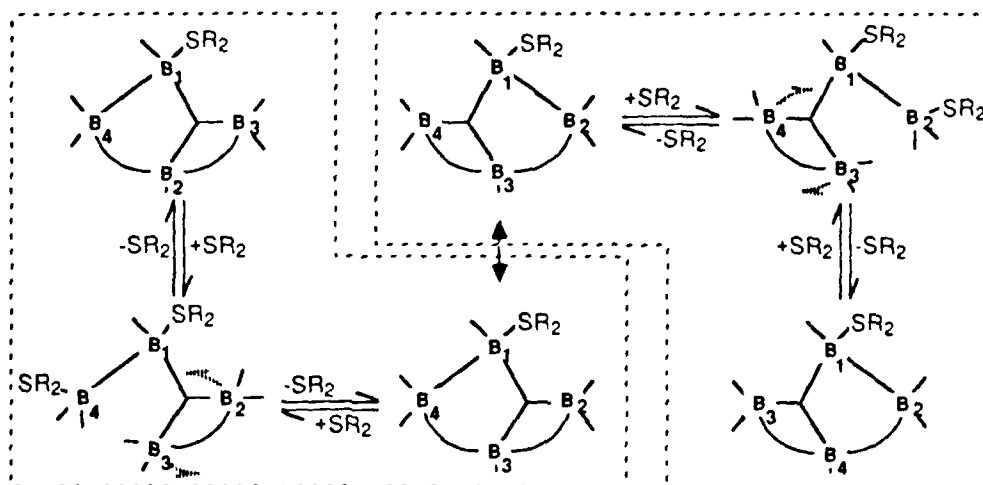


Thioethers are weaker bases than $N(CH_3)_3$ but stronger than PH_3 . Therefore, it is reasonable to assume that $B_4H_8 \cdot SR_2$ interacts with SR_2 to form an unstable bis(base) adduct:



The equivalency of the B_2 , B_3 and B_4 atoms can be achieved by the mechanism which is illustrated in Scheme 2.

Scheme 2



The above mechanism for the $B_4H_8 \cdot SR_2$ signal coalescence suggested that other B_4H_8 adducts might undergo the same type of rapid motion when dissolved in thioethers. Indeed, the $B_{2,4}$ and B_3 signals of $B_4H_8 \cdot P(CH_3)_3$ coalesced at $+20^\circ C$ in $S(CH_3)_2$ solution. Trimethylamine adduct of B_4H_8 , however, behaved differently; in dimethyl thioether its $B_{2,4}$ and B_3 signals did not coalesce up to $+30^\circ C$. Even the broadening of these signals was not observed, but an extremely broad hump (or a rise of the base line) developed in a range from 0 to -5 ppm. Recording of higher temperature spectra was prohibited by the decomposition that formed $BH_3 \cdot N(CH_3)_3$. It has been observed that, when $N(CH_3)_3$ is attached at the B_1 position of the B_4H_8 fragment, the interaction

of the B_4H_8 adduct with the second Lewis base is weak (see, for example, Equation 32) and that a soft base appears to prefer the B_1 position to the B_2 position if the choice is given. Thus, the attachment of $S(CH_3)_2$ to the B_2 position is disfavored. If $B_4H_8 \cdot N(CH_3)_3 \cdot S(CH_3)_2$ is formed, it would have $S(CH_3)_2$ and $N(CH_3)_3$ at B_1 and B_2 positions, respectively. It is possible that the broad hump at 0-5 ppm is due to the formation of this bis(base) adduct.

The complexity of base-influenced fluxionality was further observed on $B_4H_8 \cdot 2P(CH_3)_3$ and $B_4H_8 \cdot 2N(CH_3)_3$. As diagrammatically shown in Figure 3, the fluxional motion of $B_4H_8 \cdot 2P(CH_3)_3$ is slowed down in the presence of free $P(CH_3)_3$, $N(CH_3)_3$ or tetrahydrofuran, whereas that of $B_4H_8 \cdot 2N(CH_3)_3$ appears to be fast even at $-80^\circ C$ and even in the presence of free $N(CH_3)_3$. Further experimental and theoretical studies are needed for the better understanding of these phenomena.

| | Temp. | in CH_2Cl_2 | In the ligand base |
|---------------------------|-------|---------------|--------------------|
| $B_4H_8 \cdot 2N(CH_3)_3$ | High | | |
| | Low | | |
| $B_4H_8 \cdot 2P(CH_3)_3$ | High | | |
| | Low | | |

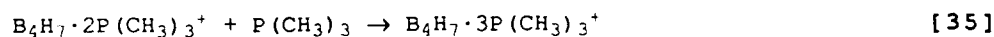
Figure 3. Diagrammatical representation of ^{11}B NMR spectra of $B_4H_8 \cdot 2N(CH_3)_3$ and $B_4H_8 \cdot 2P(CH_3)_3$.

D. Polyboron Complex Cations.

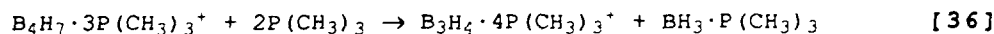
During the previous contract period, salts of the triboron complex cation $B_3H_6 \cdot 2P(CH_3)_3^+$ was isolated and characterized. In view of the possible reaction of such cations with anionic borane species to form larger boron hydride compounds, a number of polyboron cations were synthesized. A review of this new generation of compounds was presented as one of the session lectures²⁶ at the Sixth International Meeting on Boron Chemistry (IMEBORON VI), which was

held at Bechyne, Czechoslovakia in June, 1987. A reprint of the paper is attached to this report. See Reprint #8. In this section, therefore, the description is limited to the latest development that was made after the review writing.

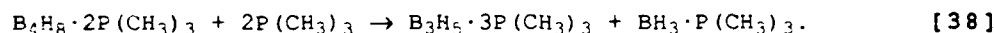
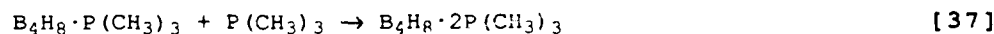
The $B_4H_7 \cdot 3P(CH_3)_3^+$ cation.^{35,36} Treatment of $B_4H_7 \cdot 2P(CH_3)_3^-$ with a molar equivalent of $P(CH_3)_3$ resulted in the formation of the $B_4H_7 \cdot 3P(CH_3)_3^+$ cation.



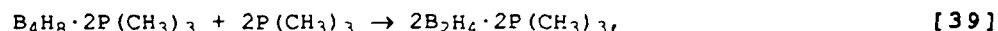
The general formula for this cation is $B_nH_{n+3} \cdot 3L^+$, and thus represents a new homologue of polyboron complex cations. The cation reacted further with $P(CH_3)_3$ to give cleavage products.



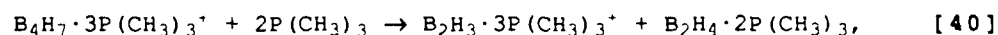
The above reactions (Equation 35 and 36) are analogous to those observed for the corresponding isoelectronic, neutral borane compounds:



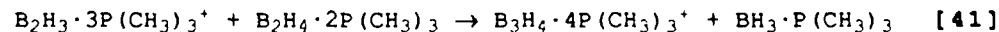
The difference between the two reaction systems is that reaction 38 is always accompanied by reaction 39.



whereas the corresponding cleavage reaction for $B_4H_7 \cdot 3P(CH_3)_3^+$,



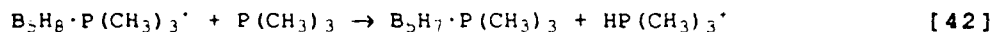
was not observed. It is possible that the reaction (Equation 40) had occurred, but that the products had undergone a reaction, in which $B_2H_4 \cdot 2P(CH_3)_3$ served as the reagent for framework expansion. See Equation 41.



Reaction of $B_5H_8 \cdot P(CH_3)_3^+$ with $P(CH_3)_3$ - Formation of $B_5H_7 \cdot P(CH_3)_3$.

Both similarities and differences between the reactions of polyboron complex cations and their corresponding isoelectronic, neutral compounds have been

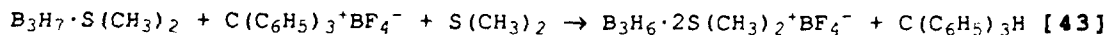
encountered, and are described in the review paper (Reprint #8). In general, $P(CH_3)_3$ either adds to the polyboron cations or cleaves the polyboron framework. However, $B_5H_8 \cdot P(CH_3)_3^+$ cation undergoes the reaction shown in Equation 42.



The newly formed, adduct $B_5H_7 \cdot P(CH_3)_3$ is characterized by its ^{11}B signals that appear at -56.3 (d, $J_{BP}=80$ Hz), -24.5 (d, BH) and -23.7 ppm (d, BH). The compound decomposes above -50 °C. The $B_5H_8 \cdot P(CH_3)_3^+$ cation is isoelectronic with B_5H_9 . The protic acid character of B_5H_9 has been demonstrated by its reaction with alkali metal hydride or ammonia to form $B_5H_8^-$.³⁷ However, the reaction of B_5H_9 with $P(CH_3)_3$ gives $B_5H_9 \cdot 2P(CH_3)_3$.³⁸ Apparently, the protonic character of the bridge hydrogen atoms in the $B_5H_8 \cdot P(CH_3)_3^+$ cation is enhanced by the ionic charge, and therefore the deprotonation is facilitated. Complete characterization of the cation including its chemical behavior is yet to be completed.

~~$B_3H_6 \cdot 2S(CH_3)_2^+ BF_4^-$~~ . Reactivities of borane compounds are often changed drastically depending upon the nature of Lewis bases involved as ligands or solvents. Having established several definable reactions involving $P(CH_3)_3$, our efforts were directed to the study of systems involving weaker Lewis bases. The synthetic study of $B_3H_6 \cdot 2S(CH_3)_2^+$ was thus initiated.

Treatment of $B_3H_7 \cdot S(CH_3)_2$ with $C(C_6H_5)_3^+ BF_4^-$ in the presence of $S(CH_3)_2$ gave the BF_4^- salt of a cation which is tentatively identified as $B_3H_6 \cdot 2S(CH_3)_2^+$.



The cation, $B_3H_6 \cdot 2S(CH_3)_2^+$, is characterized by its ^{11}B NMR signals at -26.8 and -8 ppm in a relative intensity ratio 2:1. The signal at -8 ppm is broad and assigned to the BH_2 unit. See Figure 4. The salt decomposes at room temperature.

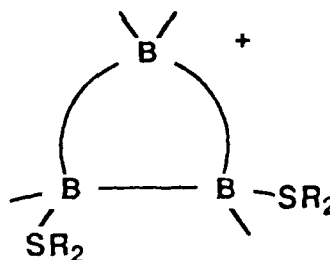
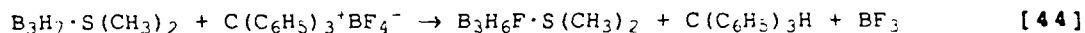


Figure 4. $B_3H_6 \cdot 2S(CH_3)_2^+$

The reaction 43 is always accompanied by a reaction which forms $B_3H_6F \cdot S(CH_3)_2$ (Equation 44).



When $B_3H_7 \cdot S(CH_3)_2$ was treated with $C(C_6H_5)_3^+BF_4^-$ at -80 °C in CH_2Cl_2 in the absence of $S(CH_3)_2$, the fluorotriborane formation (Equation 44) proceeded exclusively. Because of the weak B-S bond (relative to the B-P and B-N bonds) and the unprecedented fluoro derivative of triborane(7), the reaction chemistry of these species should be of great interest.

The fluorotriborane adduct showed the ^{11}B NMR signals at +15.5 (d, $J_{BF} \approx 65$ Hz), -19.3 and -27.2 ppm, which are assigned to the B_1 , B_3 and B_2 atoms, respectively. See Figure 5. The ^{19}F NMR signal was at -170 ppm (Reference: $CFCl_3$). The compound decomposed above -23 °C to give B_5H_9 , $BF_3 \cdot S(CH_3)_2$ and $BH_3 \cdot S(CH_3)_2$.

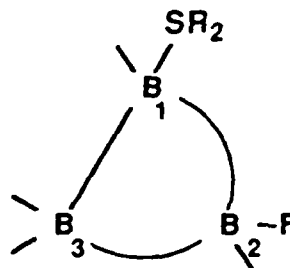


Figure 5. $B_3H_6F \cdot S(CH_3)_2$

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III. Publications and Presentation Resulting from This
Period of the ARO Supported Research

A. Publications

Reprints of the papers No.1 through No.10
are attached at the end of this report.

1. Snow, S. A.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 795. Novel Coordination of a Neutral Borane Adduct to Nickel(0). Formation of $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3]$.
2. Kameda, M.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2712. Synthesis of the Heptahydrobis(trimethylphosphine)tetraboron(1+) cation.
3. DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2871. Isolation and Characterization of Bis(trimethylamine)-Diborane(4).
4. Snow, S. A.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 3339. Synthesis and Characterization of 2-(Dichloroboryl)pentaborane(9).
5. Kameda, M.; Kodama, G. *Inorg. Chem.* **1987**, *26*, 2011. Reactions of trimethylphosphine-Pentaboranes with Trityl Cation. Formation of Octahydrobis(trimethylphosphine)pentaboron(1+) and Octahydrotrimethylphosphinepentaboron(1+) Cations.
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10. DePoy, R.E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 1836. Formation of Diboron Complex Cations.
11. Jock, C.P.; Kodama, G. *Inorg. Chem.* **1988**, *27*, in Press. Preparation and Characterization of Phosphine-Tetraborane(8).
12. DePoy, R.E.; Kodama, G. *Inorg. Chem.* **1988**. Submitted. Protic Acid Behavior of Phosphine-Triborane(7).
13. Jock, C.P.; Kameda, M.; Kodama, G. *Inorg. Chem.* Manuscript in preparation. $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ as a Reagent for Borane Cluster Expansion.

14. Kameda, M.; Driscoll, J.; Kodama, G. *Inorg. Chem.* Manuscript in preparation. Preparation and Characterization of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ and Methyl Derivatives of triboron Complex Cations.
15. Kameda, M.; Kodama, G. *Inorg. Chem.* Manuscript in preparation. New Homologs of Triboron and Tetraboron Complex Cations.
16. Shimoi, M.; Kodama, G. *Polyhedron.* Manuscript in preparation. Rapid Hydrogen Exchange Between BH_3 adducts and Hydrogen Chloride.
17. Jock, C. P.; Kodama, G. *Inorg. Chem.* Manuscript in preparation. Formation and Characterization of $\text{B}_2\text{H}_7^- \cdot \text{PH}_2^-$.
18. Several more manuscripts to be written up.

B. Dissertations.

1. Steven A. Snow, Ph.D. Dissertation, University of Utah, Salt Lake City, Utah, 1981. I. Metal Complexes of Bis(trimethylphosphine)-Diborane(4). II. Synthesis and Characterization of 2-(Dichloroboryl)pentaborane(9).
2. Rosemarie E. DePoy, Ph.D. Dissertation, University of Utah, Salt Lake City, Utah, 1987. Chemistry of Lower Borane Compounds: Syntheses and Reaction Chemistry Involving Adducts of Diborane(4) and Triborane(7).
3. Christopher P. Jock, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1987. Preparation and Characterization of Phosphine-Tetraborane(8).

C. Presentations.

1. "Chemistry of Lower Boranes Involving Trimethylphosphine." G. Kodama. Professor Anton Burg's Half-Century of Boron Research Symposium. Donald P. and Katherine B. Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA. March 14-15, 1985.
2. "Things That Followed the Isolation of Amine-Tetraborane(8): The Grapes Are Sweet." G. Kodama. Chemistry: The Landscape and the Horizon. Chemistry Symposium to Honor Professor William N. Lipscomb. University of Denver, Denver, CO. June 9-11, 1985.
3. "Synthesis and Structures of Di-, Tetra- and Pentaboron Complex Cations." M. Kameda and G. Kodama. 40th ACS Northwest Regional Meeting, Sun Valley, Idaho, June 19-21, 1985. Paper No. 59.
4. "Isolation and Reactions of Bis(trimethylamine)-diborane(4)." R.E. DePoy and G. Kodama. 40th ACS Northwest Regional Meeting, Sun Valley, Idaho, June 19-21, 1985. Paper No. 60.
5. "Boron Hydride Adducts as Coordinating Ligands for Metals." R.W. Parry, G. Kodama and S.A. Snow. 40th ACS Northwest Regional Meeting, Sun Valley, Idaho, June 19-21, 1985. Paper No. 155.

6. "Polyboron Complex Cations - A Recent Development in the Lower Borane Chemistry." M. Kameda, R.E. Depoy and G. Kodama. The Sixth International Meeting on Boron Chemistry, Bechyne, Czechoslovakia, June 20-26, 1987.
7. "Formation of Tris(trimethylphosphine)heptahydrotetraboron(1+) Cation." M. Kameda, G. Kodama and R. W. Parry. The 1st Meeting on Boron Chemistry, U.S.A., Houston, Texas, April 10-13, 1988.
8. "Thioether Adducts of Triborane(7) and Tetraborane(8)." M. Ishii and G. Kodama. The 3rd Chemical Congress of North America & the 195th Meeting of the American Chemical Society, Toronto, Canada, June 5-10, 1988. Paper No. INOR 75.

IV. Participating Scientific Personnel

| | |
|----------------------|--|
| Parry, Robert W. | Principal Investigator Distinguished Professor of Chemistry |
| Kodama, Goji | Principal Investigator Research Professor |
| DePoy, Rosemarie E. | Graduate Student |
| Helstrom, Arlee L. | Graduate Student |
| Higashi, John M. | Post-Doctoral Fellow |
| Ishii, Minoru | Post-Doctoral Fellow |
| Jock, Christopher P. | Graduate Student |
| Kachensky, David F. | Post-Doctoral Fellow |
| Kameda, Mitsuaki | Research Associate |
| Shimoi, Mamoru | Research Fellow |
| Snow, Sarah S. | Graduate Student |
| Snow, Steven A. | Graduate Student |

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Novel Coordination of a Neutral Borane Adduct to Nickel(0). Formation of $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$

Sir:

Recently we reported¹ the synthesis and characterization of Zn(II) and Cu(I) complexes of bis(trimethylphosphine)-diborane(4), $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$. These compounds represented the first examples of metal complexes of a neutral borane adduct and featured coordination of the boron hydride ligand to the metal via two B-H-M bridges. This *bidentate-bridging* mode of coordination had previously been observed primarily in complexes of the BH_4^- ,² $\text{B}_2\text{H}_6^{2-}$,^{3,4} and $\text{B}_3\text{H}_8^{5,6}$ borane anions. Of these complexes of the anions, only a few are known to have the metal center in oxidation state zero.⁷ So far there have not been reports of these anions complexing to the Ni(0) center. We now report that the neutral borane adduct $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ will react with $\text{Ni}(\text{CO})_4$ to form a stable, isolable Ni(0) complex, $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$, which contains two B-H-M bridge bonds to the Ni(0) center.

The new nickel complex was formed by the direct reaction of $\text{Ni}(\text{CO})_4$ and $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ in dichloromethane at room temperature according to eq 1. To drive the reaction forward, the



carbon monoxide had to be removed from the reaction system as it was produced, until approximately 80-85% of the reaction was complete. The product could be isolated by adding pentane to its cold, concentrated toluene solution and thus precipitating it as a green-yellow solid that was reasonably air stable at room temperature. Dichloromethane solutions of the isolated compound, however, decompose above -10 °C to unidentifiable products. Attempts to force reaction 1 to completion by further removal of carbon monoxide beyond the extent indicated above resulted in the sudden decomposition of the product, with deposition of nickel metal in the reaction system.

The reaction stoichiometry (observed: CO evolved:complex formed = 2:1) and the elemental analysis of the compound (Anal. Found: Ni, 19.9. Calcd: Ni, 20.1) supported the formula $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$ for the new nickel complex. The ¹¹B

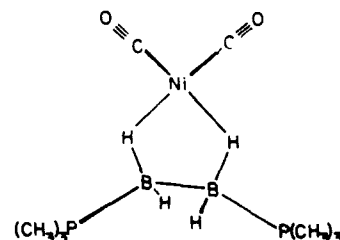


Figure 1. Proposed structure of $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$.

NMR spectrum of the compound features a broad signal at -44.1 ppm [$\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ standard] with a triplet structure, which is similar to the ¹¹B NMR signal of the previously characterized $\text{CuI}[\text{P}(\text{C}_6\text{H}_5)_3][\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$ complex.¹ The ¹H (¹¹B-spin decoupled) spectrum shows three signals in a 18:2:2 relative intensity ratio. The most intense signal, at +1.26 ppm, is a doublet (²J_{PH} = 8.5 Hz) and is assignable to the methyl protons of the trimethylphosphine groups. The signal at -0.21 ppm is assigned to the terminal hydrogens bound to boron and that at -2.42 ppm to the hydrogens in the two B-H-Ni bridges. Thus, the NMR data support the structure shown in Figure 1, in which the $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ ligand is complexed in the bidentate-bridging mode similar to that in the Zn(II) and Cu(I) complexes previously characterized.¹

The infrared and mass spectral data gave further support to the above structural assignment. The major features of the infrared spectrum include a sharp, strong absorption at 2322 cm⁻¹ (terminal B-H stretch), a broad strong absorption at 1895 cm⁻¹ (B-H-M), and two CO bands at 1933 and 1909 cm⁻¹. The distribution and intensities of absorptions below 1700 cm⁻¹ are very similar to those of the Zn(II) and Cu(I) complexes of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$.¹ In the mass spectrum, the parent ion cluster is seen centered at *m/z* = 292 with separate clusters for successive losses of CO at *m/z* = 264 and 236.

When $\text{Ni}(\text{CO})_2[\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3]$ was treated with anhydrous hydrogen chloride, the B-B bond of the borane ligand was cleaved, producing $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ and $\text{BH}_2\text{Cl}\cdot\text{P}(\text{CH}_3)_3$. Treatment of a dichloromethane solution of the compound with excess carbon monoxide at room temperature caused rapid displacement of the $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ ligand, reaffirming the equilibrium nature of the $\text{Ni}(\text{CO})_4\text{-B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ reaction system. Furthermore, the reactions of the complex with a series of phosphines of different coordinative strength gave an insight into the strength of binding of the $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ ligand to the Ni(0) center: The ligand is displaced rapidly and completely by PF_3 at -80 °C, rapidly by $\text{P}(\text{C}_6\text{H}_5)_3$ at -40 °C, and slowly by PH_3 at -20 °C. Thus, the bidentate coordinative bond of this borane ligand is not very strong, and this property can be utilized for the facile, low-temperature preparation of certain Ni(0) complexes with the formula $\text{Ni}(\text{C}\equiv\text{O})_2\text{L}_2$. The above reactions yielded $\text{Ni}(\text{CO})_2(\text{PF}_3)_2$, $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$, and $\text{Ni}(\text{CO})_2(\text{PH}_3)_2$, respectively. Further study

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on the complexes of the $B_2H_4 \cdot 2P(CH_3)_3$ ligand involving other metals in oxidation state zero and their reaction chemistry is in progress, and the results will be reported elsewhere at a later date.

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Registry No. $Ni(CO)_2[B_2H_4 \cdot 2P(CH_3)_3]$, 94890-80-9; $Ni(CO)_4$, 13463-39-3; $BH_3 \cdot P(CH_3)_3$, 1898-77-7; $BH_2Cl \cdot P(CH_3)_3$, 64160-46-9; $Ni(CO)_2(PF_3)_2$, 13859-78-4; $Ni(CO)_2[P(C_6H_5)_3]_2$, 13007-90-4; $Ni(CO)_2(PH_3)_2$, 83365-30-4.

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**Synthesis of the
Heptahydrobis(trimethylphosphine)tetraboron(1+) Cation**

Mitsuaki Kameda and Goji Kodama*

Received December 11, 1984

The triboron complex cation $B_3H_6 \cdot 2P(CH_3)_3^{+1}$ represents the first example of Lewis base attached boron cluster cations, and some novel reactions involving this cation were reported recently.^{2,3} While its reaction chemistry continues to be an intriguing subject of study, the search for other members of the polyboron complex cation family is of natural interest. Several members are known to exist in each of the related, neutral ($B_nH_{n+4} \cdot L$, L = Lewis base) and anionic ($B_nH_{n+5}^-$) boron hydride families.⁴

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- (1) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.
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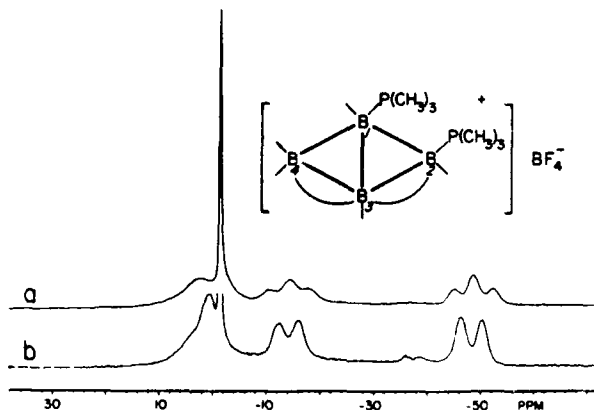


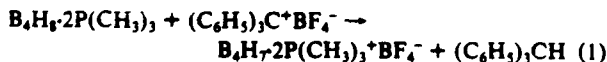
Figure 1. ^{11}B NMR (32.1 MHz) spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$ in CH_2Cl_2 at ambient temperature: (a) normal spectrum; (b) proton-spin-decoupled spectrum.

The above mentioned triboron cation was prepared by the addition of the cationic species BH_2^+ to the neutral borane adduct $\text{B}_2\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3$.¹ Another borane cation of different type, B_3H_8^+ , was prepared also by the addition of the H^+ cation to B_3H_{10} .⁵ An alternative approach to the synthesis of a cationic borane species would be the abstraction of a hydride anion (or any anionic species) from an appropriate, neutral borane compound. This method was employed in 1970 by Benjamin and co-workers⁶ for the preparation of the H_2BLL^+ cations. They treated the Lewis base adducts of borane(3) with triphenylcarbenium (trityl) cation in the presence of Lewis base L' to successfully synthesize the monoboron complex cations.

The abstraction of the hydride ion would be facilitated if the hydridic character of the hydrogen atoms in the borane compound were enhanced. Boron hydride anions represent the obvious, extreme case where H^- can be abstracted easily. With regard to the neutral borane adducts, one expects that, the stronger the donor property and the larger the number of the Lewis bases involved, the more hydridic the borane hydrogen would be. The hypophosphite-class tetraborane adduct $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$,⁷ therefore was chosen for its conversion by means of the hydride abstraction into the tetraboron complex cation. The desired cation formation occurred, and its tetrafluoroborate salt could be isolated.

Results and Discussion

Synthesis and Characterization of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$. When bis(trimethylphosphine)-tetraborane(8) was mixed with trityl tetrafluoroborate in dichloromethane, the following reaction occurred above -80°C :



The reaction was virtually quantitative. After the evaporation of the solvent, the salt of the tetraboron cation could be separated from the solid residue by washing it with toluene. The new compound is soluble in dichloromethane but insoluble in toluene. It is very sensitive to moisture. Once the compound is exposed to the slightest amount of moisture, the $\text{B}_3\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+$ cation is produced from it.

Shown in Figure 1 are the ^{11}B NMR spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$ in dichloromethane at ambient temperature. Also shown in the figure is the structure of the cation, which is proposed on the basis of the observed ^{11}B and ^{31}P NMR spectra. The sharp signal at -1.1 ppm is due to the BF_4^- anion. The multiplet signals at -48.3 and -14.2 ppm unequivocally indicate the presence of

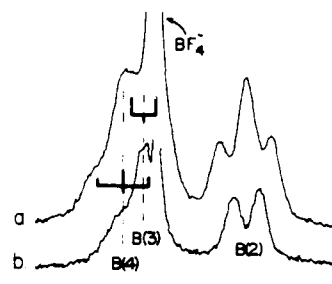
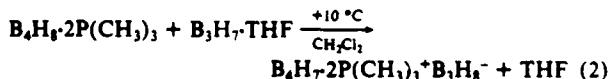


Figure 2. $+10$ to -20 ppm portions of ^{11}B NMR spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$, indicating the multiplet features of the B(3) and B(4) signals: (a) normal spectrum; (b) proton-spin-decoupled spectrum.

two different $\text{B}(\text{H})\text{P}(\text{CH}_3)_3$ moieties in the cation. The more shielded of the two is attributed to the apex boron atom (or the boron atom opposite to the $\text{B}-\text{H}-\text{B}$ bridge bonds).⁸ The broad hump, which centers around $+2$ ppm and partly overlaps with the BF_4^- signal, consists of two signals. In the ^1H -spin-decoupled spectrum (Figure 1b) the feature of two-signal overlap may be discerned. The relative intensity ratio of this hump (excluding the BF_4^- signal) to the other two $\text{B}(\text{H})\text{P}(\text{CH}_3)_3$ signals was measured to be 1.8:1.0:1.0. Shown in Figure 2 is the $+10$ to -20 ppm portion of the spectrum of a separate sample, which was recorded for a closer look at the spectral features in this region. As indicated in the figure, the broad hump consists of a triplet and a doublet (Figure 2a), each of which reduces to a singlet upon irradiation of the sample with the ^1H resonance frequencies (Figure 2b). Thus the cation is of C_1 symmetry, and assignments are made for the four signals as follows: B(1), -48.3 ppm ($J_{\text{BP}} = 126$ Hz, $J_{\text{BH}} = 106$ Hz); B(2), -14.2 ppm ($J_{\text{BP}} = 115$ Hz, $J_{\text{BH}} = 122$ Hz); B(3), $+0.75$ ppm ($J_{\text{BP}} \approx 120$ Hz); B(4), $+2.7$ ppm, ($J_{\text{BP}} \approx 120$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 121.5 MHz clearly showed two overlapping 1:1:1:1 quartet signals at -6.1 (P(2), $J_{\text{BP}} = 110$ Hz) and -4.6 ppm (P(1), $J_{\text{BP}} = 127$ Hz). Thus, like those of the trio B_3H_8^- , $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$, and $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$, the structures of B_4H_8^- ,⁹ $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$,² and $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+$ are closely related. Replacement of H^- by $\text{P}(\text{CH}_3)_3$ at the 1-position of the B_4H_8^- structure, followed by the same replacement at the 2-position of the resulting $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$, completes the structures of the tetraboron trio.

Octahydrotriborate(1-) Salt of the Tetraboron Cation. Bis-(trimethylphosphine)-tetraborane(8) reacted with tetrahydrofuran-triborane(7) to give the B_3H_8^- salt of the tetraboron complex cation.

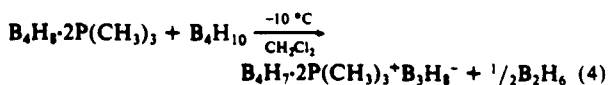


The reaction proceeded at a moderate rate. The B_3H_8^- salt, however, converted slowly at room temperature into the trimethylphosphine adducts of B_4H_8 and B_3H_7 .



This exchange of $\text{P}(\text{CH}_3)_3$ for H^- between the cation and the anion indicates that the hydride abstraction (eq 2) is the process that is kinetically favored over the alternative phosphine abstraction.

Tetraborane(10) reacted with $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ to give the B_3H_8^- salt also.



Here again, the hydride abstraction is the kinetically favored process. This and the above reaction of $\text{B}_3\text{H}_7\cdot \text{THF}$ (eq 2) contrast with the reaction of B_2H_6 with $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$.²

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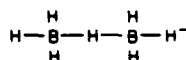
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in which no evidence for the formation of the B_2H_7^- or BH_4^- salt of the $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+$ cation could be found while the reaction was monitored with the use of a ^{11}B NMR spectrometer, starting at -80°C .

Diborane(6) or tetrahydrofuran-borane(3) is capable of abstracting hydride from borane compounds. The reactions of $\text{BH}_3\cdot \text{N}(\text{CH}_3)_2^-$, $(\text{BH}_3)_2\text{SC}_2\text{H}_5^-$, and $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3^-$ with B_2H_6 give $\mu\text{-(CH}_3)_2\text{N}\cdot\text{B}_2\text{H}_5$,¹⁰ $\mu\text{-(C}_2\text{H}_5)_2\text{SB}_2\text{H}_5$,¹¹ and $\text{B}_4\text{H}_8\cdot \text{P}(\text{H}_3)_3$,¹² respectively, the BH_4^- salt of the Na^+ or K^+ cation being another product in each of the reactions. The formation of the B_2H_7^- anion¹³



offers an example of the significant interaction of the BH_3 acid with the hydridic hydrogens in BH_4^- . Indeed, it would be this type of B-H-B interaction that makes the hydride transfer kinetically favorable over the phosphine transfer in the above reactions (eq 2 and 4). That is, the terminal hydrogen atoms are exposed to the attacking borane acids for the facile interaction. Apparently, the acid strength or the hydride affinity of B_3H_7 and B_4H_{10} is strong enough to effect the hydride transfer to these attacking acids after the intermediates involving the B-H-B bonds are formed, whereas the hydride affinity of B_2H_6 or BH_3 is not high enough to allow the H^- transfer to occur. A similar explanation based on the hydride affinity difference was used to account for the strikingly different behavior between the B_3H_8^- salt of the $\text{B}_2\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$ cation and the B_2H_7^- salt of the same cation.³

Experimental Section

General Data. Conventional vacuum-line techniques were used throughout for the handling of volatile and air-sensitive compounds. The sources of B_2H_6 , B_4H_{10} , CH_2Cl_2 , and tetrahydrofuran are described elsewhere.² Toluene (reagent grade) was refluxed and stored over CaH_2 . Triethyl tetrafluoroborate (Alfa Products) was dried on the vacuum line before use. The NMR spectra were recorded on a Varian XL-100-15 spectrometer operating in the FT mode. A Varian SC-300 spectrometer was used to obtain the ^{19}P NMR spectra. The shifts were expressed with respect to $\text{BF}_3\cdot \text{O}(\text{C}_2\text{H}_5)_2$ and 85% orthophosphoric acid. Low-field shifts were taken positive.

Synthesis of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$. From 0.53 mmol of B_3H_7 and 1.66 mmol of trimethylphosphine, with the use of a sublimation-sampling apparatus,¹⁴ $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ was prepared⁷ and was placed in a 22-mm-o.d. reaction tube equipped with a 24/40 inner joint and a 10-mm-o.d. side tube (for the later introduction of the $\text{C}(\text{C}_6\text{H}_5)_3^+\text{BF}_4^-$ sample into the reaction tube). The adduct was dissolved in 3.5 mL of CH_2Cl_2 ,

and the solution was frozen at -197°C . A 0.535 mmol sample of $\text{C}(\text{C}_6\text{H}_5)_3^+\text{BF}_4^-$ was placed above the frozen solution through the side tube under the atmosphere of dry nitrogen gas, the side-tube was sealed off, and the vessel was evacuated. The reaction occurred at -80°C as evidenced by the change of color of the solution from a dark yellow to a pale brown in 10 min. Pieces of solid (the triethyl salt) were still seen. The mixture was allowed to warm stepwise to -60 , -45 , -23 , and 0°C and room temperature while it was stirred for 10 min at each of the temperatures. The solution was clear, and no noncondensable gas was found. Then the solvent was pumped out, and the tube containing an off-white solid residue was transferred to a filtration unit. The solid was washed with toluene until nothing could be extracted, and then the remaining solid was washed into another tube with CH_2Cl_2 . Removal of the solvent from the solution by evaporation gave a white solid of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$. Anal. Calcd for $\text{B}_4\text{C}_6\text{H}_{12}\text{P}_2\text{F}_4$: B, 18.7%. Found: 18.4%.

Reaction of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ with $\text{B}_3\text{H}_7\cdot \text{THF}$. A 0.54-mmol sample of solid $\text{B}_3\text{H}_7\cdot \text{THF}$ was prepared¹⁵ in a 19-mm-o.d. tube equipped with a standard taper inner joint, and the adduct was dissolved in 1.5 mL of CH_2Cl_2 . A 0.53-mmol sample of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ was prepared in the same manner as described above, and placed in a 9-mm-o.d. tube equipped with a stopcock and an outer joint. The tube containing the $\text{B}_3\text{H}_7\cdot \text{THF}$ solution was attached to the 9-mm tube through the joints, the system was evacuated, and the solution was poured onto the $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ sample at -80°C . The $\text{B}_3\text{H}_7\cdot \text{THF}$ that was adhering on the wall was gathered above the solution in the 9-mm tube by cooling the lower end of the tube to -197°C . The mixture was mixed to a uniform solution at -80°C , placed in the cold probe of the NMR spectrometer, and examined for its change, starting at -80°C .

No change could be seen until the temperature was raised to -10°C , where a very weak signal of B_2H_6^- could be detected. At this temperature, the progress of the reaction was very slow. At $+10^\circ\text{C}$ the growth of the B_3H_7^- and $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+$ signals was reasonably fast. At $+20^\circ\text{C}$ the reaction was almost complete in 5 min. At this time the signals of $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$ could be detected. The signals of $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$ grew steadily at the expense of the $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+\text{B}_2\text{H}_6^-$ signals, and 1.5 h later the spectrum showed that the solution contained $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$ in a 1:1 molar ratio, the minor contaminants being B_2H_6 , $\text{BH}_3\cdot \text{P}(\text{CH}_3)_3$, $\text{B}_2\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$, and B_3H_7^- .

Reaction of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ with B_4H_{10} . A 1.1-mmol sample of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ was prepared in a 10-mm-o.d. tube equipped with a stopcock, and the adduct was dissolved in about 2 mL of CH_2Cl_2 . A 1.1-mmol sample of B_4H_{10} was condensed in the tube and was mixed into the solution at -80°C . The change in the solution was monitored on the NMR spectrometer, starting at -80°C .

No change could be detected until the solution was warmed to -20°C where the signals of B_3H_8^- and $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+$ began to appear. At -10°C the reaction was fairly fast, and the B_2H_6 signal grew. At $+20^\circ\text{C}$ the $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3^+\text{B}_2\text{H}_6^-$ formation was fast and appeared to be completed in a few minutes. At this time the weak signals of $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$ were present in the spectrum of the solution. Minor signals due to B_3H_7 and $\text{BH}_3\cdot \text{P}(\text{CH}_3)_3$ were detected also.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-81-K-0101.

Registry No. $\text{B}_4\text{H}_8\cdot 2[\text{P}(\text{CH}_3)_3]^+\text{BF}_4^-$, 97042-31-4; $\text{B}_4\text{H}_8\cdot 2[\text{P}(\text{CH}_3)_3]$, 66750-83-2; $\text{B}_3\text{H}_8\cdot 2[\text{P}(\text{CH}_3)_3]^+$, 97012-35-6; $\text{B}_3\text{H}_7\cdot \text{THF}$, 52842-96-3; $\text{B}_4\text{H}_8\cdot 2[\text{P}(\text{CH}_3)_3]^+\text{B}_2\text{H}_6^-$, 97012-37-8; $\text{B}_4\text{H}_8\cdot \text{PMe}_3$, 71749-92-3; $\text{B}_3\text{H}_7\cdot \text{PMe}_3$, 97012-38-9; B_4H_{10} , 18283-93-7.

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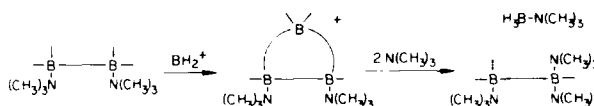
Isolation and Characterization of Bis(trimethylamine)-Diborane(4)

Sir:

We wish to report that bis(trimethylamine)-diborane(4) has been isolated as a sublimable solid. The trimethylamine adducts of many borane fragments are well-known; however, the amine adduct of the second simplest borane fragment B_2H_4 was not reported previously in the literature. Apparently in the past, the compound was overlooked in the products of certain reactions that should have contained the adduct,¹ or it was not formed by the reactions that were chosen for its synthesis.² In general, reports on nitrogen base adducts of diborane(4) have been scarce, and characterizations of the compounds have not been complete.³ On the other hand, the B_2H_4 adducts of $P(CH_3)_3$,^{4,5} $P(C_6H_5)_3$,⁶ PF_2X ($X = H$,⁷ $N(CH_3)_2$,⁷ F ,⁸ Cl ,⁹ and Br), and CO ¹⁰ have been isolated and characterized. Recent study in this laboratory on the reaction chemistry of $B_2H_4 \cdot 2P(CH_3)_3$ revealed novel aspects of this compound. These included the formation of a triboron complex cation,¹¹ the chelation to metal centers through two $B-H \rightarrow M$ bridge bonds,¹² and the framework expansion of borane compounds.^{11,13,14} These new developments involving $B_2H_4 \cdot 2P(CH_3)_3$ prompted us to investigate the nature of the trimethylamine analogue of the B_2H_4 adduct and led to the isolation of the once elusive trimethylamine adduct of diborane(4). The behavior of the new adduct toward acids paralleled that of $B_2H_4 \cdot 2P(CH_3)_3$. Yet, certain chemical properties of some of its derivatives appeared to differ from those of the trimethylphosphine analogue. A brief description of one such notable difference is included also in this communication.

Treatment of tetrahydrofuran-triborane(7) with excess tri-

Scheme 1



methylamine in dichloromethane resulted first in the formation of trimethylamine-triborane(7) at $-80^\circ C$, and then, when the reaction mixture was warmed to $0^\circ C$, the cleavage of the triborane framework slowly occurred to give $B_2H_4 \cdot 2N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3$. Typically, a 0.5-mmole quantity of $B_3H_7 \cdot THF$ was dissolved in about 1 mL of CH_2Cl_2 and was allowed to react with 2.0 mmole of $N(CH_3)_3$ at room temperature for 15 min. After removal of the solvent by evaporation, most of the $BH_3 \cdot N(CH_3)_3$ in the solid residue could be removed by sublimation at $0^\circ C$ under vacuum, and then the remaining solid was sublimed at room temperature onto a cold finger (near $0^\circ C$) to obtain a pure sample of $B_2H_4 \cdot 2N(CH_3)_3$. The yield was virtually quantitative. The mass spectrum of the compound (EI, 17 eV) showed the parent ion cluster in the range m/z 142–145, which corresponds to the formula $B_2H_4 \cdot 2N(CH_3)_3$. The NMR shift values were -3.5 ppm for ^{11}B [$BF_3 \cdot O(C_2H_5)_2$ reference] and 2.45 and 1.67 ppm for the methyl and borane protons, respectively. The ^{11}B -spin-coupled 1H signal was broad with a doublet feature, which collapsed to a singlet upon irradiation with the ^{11}B resonance frequency.

The new bis(trimethylamine) adduct is inert to both trimethylamine and ammonia. However, trimethylphosphine displaces one of the two amine ligands from $B_2H_4 \cdot 2N(CH_3)_3$ readily above $0^\circ C$ to give $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$. NMR shifts for $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$: ^{11}B , -2.9 (B_N) and -37.0 ppm (B_P); 1H , 2.52 (H_{C-N}), 1.14 (H_{C-P} , $^2J \approx 9$ Hz), 1.75 (H_{B-N}), and 0.03 ppm (H_{B-P} , $^2J \approx 17$ Hz). The second amine ligand is resistant to this displacement. Thus, only about 15% of the original amount of the adduct was converted into $B_2H_4 \cdot 2PMe_3$ when a solution of $B_2H_4 \cdot 2N(CH_3)_3$ in trimethylphosphine was kept at room temperature for about 3 h. The bis(trimethylamine) adduct of B_2H_4 is reactive toward acids and is cleaved by hydrogen chloride to form $BH_3 \cdot N(CH_3)_3$ and $BH_2Cl \cdot N(CH_3)_3$. When treated with B_2H_6 or B_4H_{10} , it gave a new triboron complex cation, $B_3H_6 \cdot 2N(CH_3)_3^+$, the counteranion being $B_2H_7^-$ or $B_4H_{10}^-$. See the first step in Scheme 1. NMR shift data for the $B_3H_6 \cdot 2N(CH_3)_3^+$ cation: ^{11}B , -9.7 (BH_2) and -15.8 ppm (B_N); 1H , 2.73 (H_C) and 1.93 ppm (H_B). Apparently, migration of the borane hydrogen atoms is rapid relative to the NMR time scale and the 1.93 ppm signal remains a singlet to $-90^\circ C$ in the ^{11}B -spin-decoupled spectrum. Although the $B_3H_6^+$ salt of the triboron cation is stable at room temperature, the $B_3H_7^-$ salt decomposes slowly above $0^\circ C$ and gives $B_3H_7 \cdot N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3$. The above behavior of $B_2H_4 \cdot 2N(CH_3)_3$ toward acids and the stabilities of the triboron cation salts are similar to those observed for $B_2H_4 \cdot 2P(CH_3)_3$ ⁵ and its triboron cation derivatives.¹¹ It is noted, however, that the reaction of $B_3H_6 \cdot 2N(CH_3)_3^+ B_3H_8^-$ with $N(C-$

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$\text{H}_3)_3$ proceeded in a manner which was entirely different from that of $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+\text{B}_3\text{H}_8^-$. The latter compound reacted with $\text{N}(\text{CH}_3)_3$ and gave the tetraborane(8) adduct $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3\cdot \text{N}(\text{CH}_3)_3$.¹⁵ In contrast, the treatment of $\text{B}_3\text{H}_6\cdot 2\text{N}(\text{CH}_3)_3^+\text{B}_3\text{H}_8^-$ with $\text{N}(\text{CH}_3)_3$ (1:2 molar ratio) at -20°C resulted in the abstraction of a BH_3 unit from the cation; the B_3H_8^- anion remained intact. Thus another new diboron complex cation, $\text{B}_2\text{H}_3\cdot 3\text{N}(\text{CH}_3)_3^+$, was produced.¹⁶ See the second step in Scheme I. The ^{11}B NMR signals of this diboron cation appeared as broad humps at 12.5 and -3.9 ppm with the half-height widths 300 and 450 Hz, respectively.

Thus, the isolation of $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$ not only has filled the vacancy in the list of representative compounds but also has given

an additional insight into the roles of different Lewis base ligands that are responsible for subtle reactivity differences of borane adducts. Further work on the derivative chemistry of $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$ is being pursued, and the details of the results will be reported at a later date.

Acknowledgment. We acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-85-K-0034.

Registry No. $\text{B}_3\text{H}_7\cdot \text{THF}$, 52842-96-3; $\text{BH}_3\cdot \text{N}(\text{CH}_3)_3$, 75-22-9; $\text{B}_2\cdot \text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$, 97551-45-6; $\text{B}_2\text{H}_4\cdot \text{N}(\text{CH}_3)_3\cdot \text{P}(\text{CH}_3)_3$, 97551-46-7; $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$, 67113-98-8; $\text{B}_3\text{H}_7\cdot \text{N}(\text{CH}_3)_3$, 57808-48-7; $\text{BH}_2\text{Cl}\cdot \text{N}(\text{CH}_3)_3$, 5353-44-6; B_2H_7^- , 27380-11-6; B_3H_8^- , 12429-74-2; B_2H_6 , 19287-45-7; B_4H_{10} , 18283-93-7; $\text{B}_2\text{H}_3\cdot 3\text{N}(\text{CH}_3)_3^+$, 97551-47-8.

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(16) Another diboron complex cation, $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3^+$, has been synthesized [Kameda, M.; Kodama, G. "Abstracts of Papers", 40th Northwest Regional Meeting of the American Chemical Society, Sun Valley, ID, June 1985; No. 59].

Synthesis and Characterization of 2-(Dichloroboryl)pentaborane(9)[†]

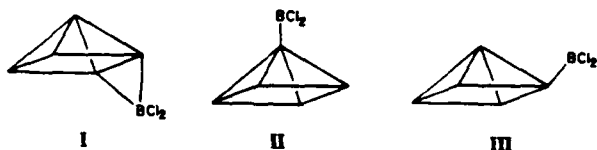
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2-(Dichloroboryl)pentaborane(9), 2-(Cl₂B)B₅H₉, was synthesized by the treatment of μ -(Cl₂B)B₅H₉ with ether (Me₂O, Et₂O, or tetrahydrofuran) followed by the reaction of the resulting 2-(Cl₂B-OR₂)B₅H₉ with BX₃ (X = Cl or F). The new compound was characterized by its ¹¹B and ¹H NMR, mass, and IR spectra. Thus, the syntheses of all three possible isomers of (dichloroboryl)pentaborane(9), μ -, 1-, and 2-isomers, were completed. The new isomer reacted with dimethyl ether, diethyl ether, or tetrahydrofuran to form a 1:1 adduct that was undissociated at room temperature. Ethylene inserted into the terminal B-B bond of the isomer to give 2-(Cl₂BC₂H₄)B₅H₉, and bromine cleaved the B-B bond to give 2-BrB₅H₉ and boron trihalides. The compound was inert to hydrogen chloride. The above conversion of μ -(Cl₂B)B₅H₉ into the 2-derivative of pentaborane as the result of the ether treatment was compared with the similar conversion of the group 14 element derivatives and was contrasted with the conversion of μ -[(CH₃)₂B]B₅H₉ into a hexaborane(10) derivative.

Introduction

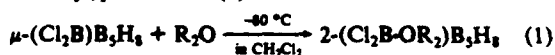
Earlier, we reported the synthesis and characterization of μ -(dichloroboryl)pentaborane(9).¹ This compound featured a dichloroboryl (BCl₂) fragment bridging two of the basal boron atoms of the pentaborane framework. (See structure I.) Sub-



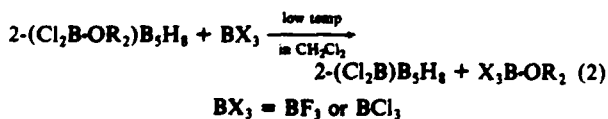
sequently, Gaines and co-workers² reported the synthesis and characterization of the isomeric compound 1-(dichloroboryl)pentaborane(9) (structure II). This compound was unique in that a trigonal boron moiety was σ -bonded to a boron atom in a boron hydride cluster. Indeed, this compound was the first example of BX₂ substitution at the terminal position of the pentaborane(9) framework. We now report the synthesis and characterization of a third isomer of (dichloroboryl)pentaborane(9), 2-(Cl₂B)B₅H₉. This isomer, shown as structure III, contains a similar, discrete boron-boron σ -bond at a basal position of the pentaborane framework. This study thus concludes the isolation of all three possible isomers of (dichloroboryl)pentaborane(9).

Results and Discussion

A. Synthesis of 2-(Cl₂B)B₅H₉. 2-(Dichloroboryl)pentaborane(9) was formed by a two-step process starting with μ -(dichloroboryl)pentaborane(9):



R₂O = Me₂O, Et₂O, or tetrahydrofuran (THF)



In eq 1, the BCl₂ group migrated from its original bridge position to a basal terminal position upon the reaction with ether. Characterization of 2-(Cl₂B-OR₂)B₅H₉ is described in part D of this section. Treatment of the ether complex of 2-(dichloroboryl)pentaborane(9) with an excess of BX₃ in dichloromethane liberated 2-(Cl₂B)B₅H₉, which was recovered in a 65–70% yield based on the original amount of μ -(Cl₂B)B₅H₉ used. For ease of isolation of 2-(Cl₂B)B₅H₉, BCl₃ was the preferred choice of Lewis acid to BF₃, because of the lower volatility of its ether

adducts relative to that of the BF₃ etherates. The compound 2-(Cl₂B)B₅H₉ was isolated as a volatile, colorless liquid that yellowed on standing at room temperature in vacuo. It was extremely sensitive to water and air and required exhaustive flame-drying of the high-vacuum apparatus to prevent immediate formation of B₅H₉ and a nonvolatile white solid. Although it appeared reasonably stable at room temperature up to 1 week in dilute dichloromethane solutions, most solutions of this compound slowly turned yellow upon long standing at room temperature and B₅H₉ was detected in the ¹¹B NMR spectra of these solutions.

B. Characterization of 2-(Cl₂B)B₅H₉. **Mass Spectrum.** The mass spectrum of 2-(Cl₂B)B₅H₉ displayed a cluster of peaks around *m/z* 143, with the highest mass cutoff at *m/z* 148, which corresponded to the formula ¹¹B₅¹H₉³⁷Cl₂. Other significant peak clusters in the spectrum included *m/z* 58–63 and 80–85, corresponding to B₅H₉⁺ and BCl₂⁺, respectively. Thus, it appeared that the facile dissociation of the boryl group in the spectrometer was similar to the case of the μ -(Cl₂B)B₅H₉ isomer.¹

NMR Spectra. The ¹¹B and ¹H NMR data for 2-(Cl₂B)B₅H₉ are listed in Table I along with those for other new, related compounds, and the ¹¹B spectra are shown in Figure 1. The doublet signal at –50.3 ppm can be assigned to the apex B(1) atom, and the two doublets at –11.8 and –7.8 ppm in an approximately 2:1 intensity ratio are assigned to the B(3,5) and B(4) atoms, respectively. The signal of the trigonal boron atom in the –BCl₂ moiety appears at +67.5 ppm with a *J*_{B(1)B(2)} value of 106 Hz. The signal of the B(2) atom, which is expected to be a broad quartet also, is overlapped by the B(3,5) signal, and only its high-field end is discernible in the ¹H-spin-decoupled spectrum (see Figure 1). The ¹¹B-spin-decoupled ¹H NMR spectrum shows the presence of two signals in a 1:1 intensity ratio in the bridge hydrogen region. Thus, the NMR data are consistent with the structure of 2-(Cl₂B)B₅H₉, which is schematically indicated in the figure. It is noted that, although the terminal ¹¹B–¹¹B coupling constant (106 Hz) is in the range (79–151 Hz) that has been found for the other compounds,³ the Kroner and Wrackmeyer correlation predicts^{3,4} a value of 86.2 Hz for the ¹¹B–¹¹B coupling constant. The assumptions made for the calculation were that the –BCl₂ moiety is hybridized sp² and the hybridization of the B(2) atom in 2-(Cl₂B)B₅H₉ is the same as that in 2,2'-(B₅H₉)₂, which is deduced from the observed B(2)–B(2') coupling constant 79.4 Hz.³ The disagreement between the observed and calculated values is considerable. It has been shown³ that the same treatment for the terminal ¹¹B–¹¹B coupling constant for 1-(Cl₂B)B₅H₉, with the assumptions similar to the above, gives 118.8 Hz, which is in good agreement with the observed value 124 Hz. The cause of this discrepancy between the two systems is not immediately obvious.

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 10, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Table I. ^{11}B and ^1H NMR Data for $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ and Related Compounds

| compd | ^{11}B Shifts (ppm) and Coupling Constants (Hz) | | | | | | | | | |
|--|--|-----------------|-------|-----------------------------|--------|-----------------|----------------------|-----------------|-------|-----------------|
| | B(1) | | B(2) | | B(3,5) | | B(4) | | B(6) | |
| | shift | J_{BH} | shift | J_{BH} | shift | J_{BH} | shift | J_{BH} | shift | J_{BB} |
| $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ | -50.3 | 178 | -13.3 | | -11.8 | 160 | -7.8 | 165 | +67.5 | 106 |
| $2-(\text{Cl}_2\text{B}-\text{O}(\text{CH}_3)_2)_2\text{B}_2\text{H}_6$ | -51.7 | 171 | -5.9 | | -13.6 | 158 | (-13.6) ^a | (158) | +11.3 | <i>b</i> |
| $2-(\text{Cl}_2\text{B}-\text{O}(\text{C}_2\text{H}_5)_2)_2\text{B}_2\text{H}_6$ | -52.3 | 165 | -4.4 | | -14.3 | 159 | (-14.3) ^a | (159) | +7.2 | <i>b</i> |
| $2-(\text{Cl}_2\text{B}-\text{OC}_2\text{H}_5)_2\text{B}_2\text{H}_6$ | -51.2 | 169 | -3.1 | | -12.9 | 159 | (-12.9) ^a | (159) | +8.4 | <i>b</i> |
| $2-(\text{Cl}_2\text{BC}_2\text{H}_4)_2\text{B}_2\text{H}_6$ | -52.5 | 172 | +1.9 | | -13.8 | 156 | -18.2 | 156 | +62.0 | |
| $2-(\text{Cl}_2\text{B}(\text{OC}_2\text{H}_5)_2\text{C}_2\text{H}_4)_2\text{B}_2\text{H}_6$ | -52.9 | 171 | +3.8 | | -14.6 | 160 | -19.7 | 157 | +14.1 | |
| $\mu-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6^c$ | -34.2 | 185 | -4.5 | 185 [for B(2,3) and B(4,5)] | | | | | +74.8 | |
| $1-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6^d$ | -51.8 | | -13.1 | 160.6 [for B(2,3,4,5)] | | | | | +75.7 | 124 |

| ^1H Shifts (ppm) | | | | | | | |
|--|-------|-----------------------|--------------|--|-------|-----------------------|--------------|
| compd | H(1) | H(3,4,5) ^e | H(μ) | compd | H(1) | H(3,4,5) ^e | H(μ) |
| $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ | +0.66 | +2.78 | -1.65, -1.88 | $2-(\text{Cl}_2\text{BC}_2\text{H}_4)_2\text{B}_2\text{H}_6^f$ | +0.49 | +2.44 | -1.51, -2.21 |
| $2-(\text{Cl}_2\text{B}-\text{O}(\text{C}_2\text{H}_5)_2)_2\text{B}_2\text{H}_6^f$ | +0.31 | +2.43 | -1.82, -2.20 | | | | |

^a The B(3,5) and B(4) signals are overlapped, and the shifts are almost identical. ^b The expected quartet structure could not be observed due to the broadness of the signal. ^c Reference 1. ^d Reference 2. ^e The signals of H(3,5) and H(4) could not be resolved unequivocally due to the broadness of the signals. ^f The signals of the CH_3 and CH_2 protons in $(\text{C}_2\text{H}_5)_2\text{O}$ appeared at 1.39 and 4.14 ppm, respectively. ^g The signals of C_2H_4 protons are located in the range from 1.0 to 1.6 ppm as overlapped peaks of a second-order coupling pattern.

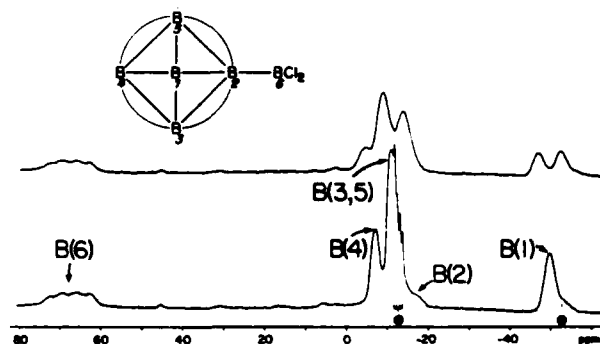
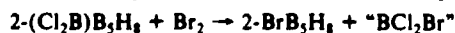


Figure 1. ^{11}B NMR spectra of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ in CH_2Cl_2 at ambient temperature: upper, normal spectrum; lower, proton-spin-decoupled spectrum; circles, signals of B_2H_6 .

C. Reactions of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ With Diethyl Ether. Treatment of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with diethyl ether at -80°C resulted in the immediate formation of the ether adduct, which was stable in a diethyl ether solution at room temperature up to 3 h. This behavior was significantly different from that observed for $1-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$, which did not appear to form an ether complex until it was heated to 50°C .² It is known that on the pentaborane framework the apical position carries the greatest negative charge.⁵ This higher charge density would decrease the acidity of the apically substituted BCl_2 moiety through an inductive effect. It is notable that there is a significantly large difference in the terminal ^{11}B - ^{11}B coupling constants of the 1- and 2-isomers (124 Hz for $1-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ vs. 106 Hz for $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$). This would imply that the B-B bond in the apical isomer is stronger and therefore more resistant to the bond deformation. It may be this high energy of reorganization that requires the heating of the mixture for the 1-isomer adduct formation. The considerable difference in the observed behavior of these two isomers toward diethyl ether, however, is not completely understood. Further study, both experimental and theoretical, is needed to elucidate this different behavior.

With Bromine. Bromine reacted with $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ at a moderate rate in a dilute dichloromethane solution at room temperature, and $2-\text{BrB}_2\text{H}_6$ and boron trihalides were produced:



The mixed halide of boron in the product underwent a dispro-

portionation reaction to produce BCl_3 and BBr_3 . This reaction can be compared with the cleavage of B_2Cl_4 with Br_2 that occurs at -23°C to form a mixture of BCl_3 and BBr_3 as the final products.⁶

With Hydrogen Chloride. No evidence for the reaction between HCl and $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ was detected when the reactants were mixed in dichloromethane and kept standing for 1 h at room temperature. This contrasted with the reactivity of the B-B bond in $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$, which was cleaved readily by hydrogen chloride at -80°C to give $(\text{CH}_3)_3\text{P}-\text{BH}_3$ and $(\text{CH}_3)_3\text{P}-\text{BH}_2\text{Cl}$.⁷ Diboron tetrachloride, however, appeared to be inert to hydrogen chloride.⁸

With Ethylene. Ethylene inserted into the B-B bond of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ to give $2-(\text{Cl}_2\text{BC}_2\text{H}_4)_2\text{B}_2\text{H}_6$. The reaction was slow at room temperature even in the presence of excess ethylene, requiring up to 2 weeks for the formation of a sufficient amount of the product. Thus, the rate of this reaction appeared to be comparable with that of $1-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with ethylene.² Insertion of ethylene into the B-B bond in B_2Cl_4 proceeds readily at -80°C .⁹ In contrast, ethylene does not react with $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$, even at room temperature.¹⁰

The ethylene insertion product, $2-(\text{Cl}_2\text{BC}_2\text{H}_4)_2\text{B}_2\text{H}_6$, was isolated as a colorless liquid, which was stable at room temperature, and was characterized by its ^{11}B and ^1H NMR spectra (Table I). The B(4) signal is shifted upfield 10 ppm from that of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$, and the B(2) signal is shifted downfield by 11 ppm. Thus, the appearance of the ^{11}B NMR spectrum resembles a superposition of the $2-\text{CH}_3\text{B}_2\text{H}_6$ and CH_3BCl_2 spectra.¹¹ The compound formed an adduct with tetrahydrofuran at the BCl_2 site, as indicated by the large upfield shift of the BCl_2 signal from +62.0 to +14.1 ppm.

The above described reactions indicate that the reactivity of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ is similar to that of the 1-isomer except for the acid behavior toward diethyl ether. These BCl_2 derivatives of pentaborane(9), however, are less reactive than B_2Cl_4 , or $(\text{Cl}_2\text{B})_2$. The reactivity pattern of another B-B-bonded compound, $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$, did not parallel that of the dichloroboryl compounds due to the entirely different environment of the boron atoms.

D. Reactions of $\mu-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with Ethers $((\text{CH}_3)_2\text{O}$, $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{CH}_2)_4\text{O}$). The reaction of $\mu-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with dimethyl ether,

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(7) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.

(8) Urry, G. In "The Chemistry of Boron and Its Compounds"; Muettterties, E. L., Ed.; Wiley: New York, 1967; Chapter 6, p 351.

(9) Urry, G.; Kerigan, J.; Parsons, T. D.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 5299.

(10) Kameda, M.; Kodama, G., unpublished observation.

(11) ^{11}B NMR shift values in ppm: for $2-\text{CH}_3\text{B}_2\text{H}_6$, B(1) -50.4, B(2) +2.2, B(3,5) -12.7, B(4) -18.1; for CH_3BCl_2 , -62.3 (taken from: Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969; pp 112, 449).

(5) See, for example: Lipscomb, W. N. In "Boron Hydride Chemistry"; Muettterties, E. L., Ed.; Academic Press: New York, 1975; p 54.

diethyl ether, or tetrahydrofuran was very rapid at -80°C in the ether itself as solvent or in dichloromethane. As the reaction was monitored by ^{11}B NMR spectroscopy, the signals of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ immediately disappeared and were replaced by the signals of $2\text{-(Cl}_2\text{B-OR)}_2\text{B}_5\text{H}_9$, which are listed in Table I. No other signals of possible intermediates could be detected. As one visualizes from the shift values in Table I, the ^{11}B NMR spectra of the etherates have a general feature that is common to that of B_5H_9 ; i.e., two distinct doublets around -52 and -13 ppm stand out conspicuously. Two major differences between the ^{11}B NMR spectra of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ and $2\text{-(Cl}_2\text{B-OR)}_2\text{B}_5\text{H}_9$, however, help to identify the ether adduct. First, the resonance of the BCl_2 boron atom has been shifted upfield more than 60 ppm. This is consistent with the conversion of a trigonally coordinated boron atom into a tetrahedrally coordinated boron atom. The second difference between the two spectra is the broadness of the two signals that are assigned to the $\text{Cl}_2\text{B-OR}_2$ boron atom and to the B(2) atom of the pentaborane framework. This wide breadth ($\nu_{1/2} \approx 350$ Hz) is consistent with the presence of the B-B single bond between the two boron atoms. The ^{11}B -spin-decoupled ^1H NMR spectra showed two signals in the region of bridge hydrogen resonances in a 1:1 intensity ratio. This is also consistent with the 2-isomer structure of the adduct, but not with the μ -isomer structure.

The above described migration of a boron atom from the bridge to the 2-position of the pentaborane(9) framework is new for group 13 element derivatives, but is reminiscent of the ether-catalyzed isomerization of group 14 element derivatives of pentaborane(9),¹² e.g.



Among the group 14 elements, carbon is unique in that the carbon-bridging derivatives of pentaborane(9) are unknown, whereas several $2\text{-(alkyl)}_2\text{B}_5\text{H}_9$ species are known.¹³ Gaines and Jorgenson suggested,¹⁴ on the basis of their observation on the reactions of B_5H_9 with allyl iodide and with benzyl bromide both in the absence of a Lewis base, that the carbon-bridging derivatives were thermodynamically unstable with respect to the corresponding 2-isomers and that the μ -derivatives isomerized to 2-derivatives at rates comparable to the rate of formation of the μ -derivatives. In our boron atom migration, the actual migrating group, $\text{-BCl}_2\text{-OR}_2$, behaved as a "quasi-alkyl" moiety and migrated rapidly to the 2-position in a manner similar to that of the alkyl analogue. The formation of $2,2'\text{-(B}_5\text{H}_9)_2$ in the reaction of $\text{K}^+\text{B}_5\text{H}_9^-$ with $2\text{-BrB}_5\text{H}_9$ can be interpreted as the result of the quasi-alkyl behavior of the basal boron atom, which may have entered first at the bridging position of the pentaborane anion framework.

While the above similarity is apparent, a striking difference is noted between $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ and $\mu\text{-[(CH}_3)_2\text{B]}_2\text{B}_5\text{H}_9$ in the results of their interactions with ether; the latter converts into 4,5-dimethylhexaborane(10) in the presence of diethyl ether.¹⁶ It is important to clarify the factors involved in these two different processes since they would be responsible for determining the route to the cage expansion or to the exocage substitution after a borane species has been placed in a bridge position of a boron hydride cluster.

Experimental Section

General Data. Conventional vacuum-line techniques were used for the handling of volatile compounds. For quantitative manipulation of (dichloroboryl)pentaborane(9) derivatives it was essential to have Teflon stopcocks fitted with Viton O-rings and removable joints with O-ring seal because of these compounds' high affinity for Apiezon M or N high-vacuum grease. Air- and moisture-sensitive solids were handled in glovebags filled with dry nitrogen gas. Boron trichloride, boron trifluoride,

dimethyl ether, ethylene (Matheson Gas Products), and bromine (Mallinckrodt Chemicals) were purified by fractional condensation on the vacuum line. Commercially obtained reagent grade diethyl ether and tetrahydrofuran were stored over LiAlH_4 , and dichloromethane was stored over molecular sieves. These liquids were distilled directly into reaction vessels on the vacuum line.

The ^{11}B and ^1H NMR spectra were recorded either on a Varian XL-100-15 spectrometer or on a Varian FT-80A spectrometer, both of which were operating in the FT mode. For the Varian XL-100-15, spectra were obtained at 32.1 and 100.1 MHz (^{11}B and ^1H , respectively), or for the FT-80A, ^{11}B spectra were acquired at 25.5 MHz. Chemical shifts were expressed with respect to $\text{BF}_3\text{O(C}_2\text{H}_5)_2$ and tetramethylsilane. The mass spectra were obtained from a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG data System 2000. Infrared spectra were acquired on a Beckman IR-20 infrared spectrometer.

Reactions of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ with Ethers (Me_2O , Et_2O , THF). Samples of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ were prepared by the literature method.¹ Reactions with ethers were performed in 9-mm-o.d. Pyrex tubes that were fitted with stopcocks. A weighed sample of the μ -isomer was condensed at the bottom of the reaction tube and was dissolved in about 2 mL of CH_2Cl_2 . Then a measured amount of the ether sample was condensed into the tube. The mixture was allowed to melt and was agitated briefly at -80°C . Then the tube was placed into the probe of the NMR spectrometer (-80°C) for the spectrum recording. The reaction of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ with the ether was rapid and essentially complete at this temperature. In any mixture where the ratio of ether to $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ was greater than 1, the ^{11}B NMR spectrum showed complete conversion of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ into $2\text{-(Cl}_2\text{B-OR)}_2\text{B}_5\text{H}_9$. In separate experiments where the ratio was less than 1, the spectrum showed the presence of both $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ and $2\text{-(Cl}_2\text{B-OR)}_2\text{B}_5\text{H}_9$. No evidence for the catalytic conversion of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ by the ethers into $2\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ was found in these experiments.

The etherates, $2\text{-(Cl}_2\text{B-OR)}_2\text{B}_5\text{H}_9$, were unstable white solids that rapidly yellowed at room temperature. When prepared from $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$, they were unstable in room-temperature solutions, and $\text{HBCl}_2\text{-OR}_2$ was the major identifiable boron-containing species in these decomposition mixtures. It was noted that when $2\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ was dissolved in diethyl ether, the resultant solution of $2\text{-(Cl}_2\text{B-OEt)}_2\text{B}_5\text{H}_9$ in the ether appeared somewhat more stable than when this compound was prepared from $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$. No $\text{HBCl}_2\text{-OEt}_2$ was detected in the ^{11}B NMR spectra of these solutions up to 4 h at room temperature, whereas within $0.5\text{--}1$ h this compound was detected in the solutions prepared from the μ -isomer.

Preparation and Isolation of $2\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$. In a typical preparation, 3.04 mmol of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ was distilled into a 22-mm-o.d. tube (as described previously) that contained a stirring bar. An 8-mL sample of dry CH_2Cl_2 was distilled into the reactor, and the two components were mixed together to form a uniform solution. The solution was cooled to -197°C to condense in 4.65 mmol of THF, and then the mixture was stirred for 30 min at -80°C to complete the reaction. To this mixture at -80°C was introduced BCl_3 (6 mmol). Approximately one-third of it was absorbed immediately. At this point solid $\text{BCl}_3\text{-THF}$ was seen precipitating from the solution. The remaining BCl_3 was condensed in at -197°C . After the solution was allowed to melt, it was stirred for 15 min at -80°C , 30 min at -45°C , and finally 20 min at 0°C . Then the volatile component was distilled out at 0°C into the vacuum line until only a fluffy white solid (primarily $\text{BCl}_3\text{-THF}$) remained behind. The last of the volatile component was pumped out at room temperature. Then the volatile component was set at -63°C and CH_2Cl_2 was pumped out. $2\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ was left behind as a white solid that melted uniformly upon warming. It was purified further by distilling out at 0°C and fractionally condensing in a -45°C trap. This procedure allowed for final removal of the high-volatility impurities. Yield: 2.10 mmol of $2\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$ or 69.1% based on the original amount of $\mu\text{-(Cl}_2\text{B)}_2\text{B}_5\text{H}_9$. The mass spectrum of the compound was obtained on the spectrometer operating at 15 eV. The observed relative intensities of the peaks in the parent cluster were as follows [m/z , observed intensity (calculated relative intensity for $\text{B}_5\text{H}_9\text{Cl}_2$): $148, 1.3$ (1.2); $147, 1.6$ (1.6); $146, 7.9$ (8.4); $145, 11.0$ (10.8); $144, 17.0$ (17.5); $143, 17.9$ (17.9); $142, 11.4$ (9.7); $141, 3.4$ (3.0); $140, 0.9$ (0.5); $139, 1.0$ (0.05)]. The agreement between the observed and calculated values is good and suggests that the successive losses of pairs of hydrogen atoms were minimal for this compound under the conditions of the spectrum acquisition. The losses of hydrogen atoms in mass spectrometer have been observed commonly for many borane compounds.¹⁷

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(14) Gaines, D. F.; Jorgenson, M. W. *Inorg. Chem.* **1980**, *19*, 1398.

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(17) Shapiro, I.; Wilson, C. O.; Ditter, J. F.; Lehman, W. J. *Adv. Chem. Ser.* **1961**, No. 32, 127. Dodds, A. R.; Kodama, G. K. *Inorg. Chem.* **1979**, *18*, 1465.

Infrared spectral data for $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ (10-cm gas cell equipped with KBr windows): 2592(s), 1785 (w, br), 1395 (m, br), 1335 (w, sh), 1187 (w), 1140 (m), 975 (sh), 937 (s), 885 (s), 839 (sh), 775 (w), 722 (w), 660 (m), 590 (w, br), 448 (w) cm^{-1} .

Reaction of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with Diethyl Ether. Into a 9-mm-o.d. tube (as described previously) were condensed at -197°C 0.2 mmol of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ and 1 mL of diethyl ether. The tube was warmed to -80°C , agitated, and then placed in the probe of the NMR spectrometer for ^{11}B analysis. At -80°C complexation of the ether had already occurred and only the signals of $2-(\text{Cl}_2\text{B}-\text{OEt}_2)\text{B}_2\text{H}_6$ were present in the spectrum.

Reaction of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with Bromine. Into a 9-mm-o.d. tube (as described previously) were condensed at -197°C 0.11 mmol of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$, 1 mL of CH_2Cl_2 , and 0.13 mmol of Br_2 (the once fractionated bromine was dried over P_2O_5 at room temperature). The mixture was warmed to -80°C with agitation and then placed in the NMR probe. At 0°C the signals of $2-\text{BrB}_2\text{H}_6$ ¹⁸ began to slowly grow, and after 1.5 h at room temperature the reaction was essentially complete. The color of the solution, which had been previously a very dark orange-red, had faded to a light yellow.

Since immediate assignment of the ^{11}B NMR signals of the products was quite difficult due to extensive peak overlap, the product mixture was fractionated on the vacuum line. When the volatile component was passed through a -63°C trap, the high-volatility (BCl_3 , BBr_3) component could be separated and identified. The low-volatility fraction consisted of $2-\text{BrB}_2\text{H}_6$ (signals at -13.2 , -20.9 , and -52.9 ppm; lit.¹⁸ ~ -11 , ~ -15 , ~ -20 , and -53.5 ppm) and possibly a small amount of $1-\text{BrB}_2\text{H}_6$ as identified by the presence of signals at -12.6 and -35.9 ppm (lit.¹⁸ -12.5 and -36.1 ppm).

Reaction of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$ with Ethylene: Synthesis of $2-(\text{Cl}_2\text{BC}_2\text{H}_4)\text{B}_2\text{H}_6$. In a typical preparation 0.75 mmol of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$

was condensed at -197°C into a 22-mm-o.d. tube (as described previously). Above the borane compound were condensed 2 mL of CH_2Cl_2 and 1.33 mmol of C_2H_4 . The mixture was then warmed to room temperature, and stirring was commenced. After 2–3 h the solution had turned slightly yellow, but this color did not appear to intensify with prolonged reaction. The stirring was continued for 2 weeks, constantly at room temperature. Then the reactor vessel was connected to the vacuum line and all of the volatiles were condensed into a -197°C trap. The new compound, $2-(\text{Cl}_2\text{BC}_2\text{H}_4)\text{B}_2\text{H}_6$, was isolated in a pure form by fractional condensation of the volatile component into a -35°C trap. The compound was a colorless liquid. The ^{11}B NMR spectra of the neat compound or its CH_2Cl_2 solution showed no sign of decomposition after 2 h of standing at room temperature. Yield: 0.14 mmol or 18.6% based on the original amount of $2-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$. The other major identifiable boron-containing product was B_2H_6 , which was identified by its ^{11}B NMR spectrum.

Reaction of $2-(\text{Cl}_2\text{BC}_2\text{H}_4)\text{B}_2\text{H}_6$ with THF. A 0.10-mmol sample of $2-(\text{Cl}_2\text{BC}_2\text{H}_4)\text{B}_2\text{H}_6$ was condensed at -197°C into a 9-mm-o.d. reaction tube (as described previously). Above this compound was condensed 1.5 mL of THF; the mixture was warmed with agitation to -80°C and then placed into the probe of the NMR spectrometer. At this point the reaction was complete, and quantitative conversion into the THF complex was indicated by the ^{11}B NMR spectrum (see Table I).

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Registry No. $\mu-(\text{Cl}_2\text{B})\text{B}_2\text{H}_6$, 81643-54-1; $2-(\text{Cl}_2\text{B}-\text{O}(\text{CH}_3)_2)\text{B}_2\text{H}_6$, 97826-06-7; $2-(\text{Cl}_2\text{B}-\text{O}(\text{C}_2\text{H}_5)_2)\text{B}_2\text{H}_6$, 97826-07-8; $2-(\text{Cl}_2\text{B}-\text{OC}_4\text{H}_9)\text{B}_2\text{H}_6$, 97826-08-9; $2-(\text{Cl}_2\text{B})\text{C}_2\text{H}_5$, 97826-09-0; $2-(\text{Cl}_2\text{BC}_2\text{H}_4)\text{B}_2\text{H}_6$, 97826-10-3; $2-(\text{Cl}_2\text{B}(\text{OC}_4\text{H}_9)\text{C}_2\text{H}_4)\text{B}_2\text{H}_6$, 97826-11-4; BCl_3 , 10294-34-5; Br_2 , 7726-95-6; C_2H_4 , 74-85-1.

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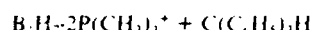
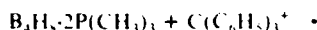
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Reactions of Trimethylphosphine-Pentaboranes with Trityl Cation. Formation of Octahydrobis(trimethylphosphine)pentaboron(1+) and Octahydro(trimethylphosphine)pentaboron(1+) Cations

Mitsuaki Kameda and Goji Kodama*

Received December 22, 1986

Earlier, we reported the synthesis of the heptahydrobis(trimethylphosphine)tetraboron(1+) cation, $B_4H_6-2P(CH_3)_3^+$. This cation was prepared by abstracting a hydride ion from $B_4H_6-2P(CH_3)_3$ with the use of triphenylcarbenium (trityl) cation.



This method of hydride abstraction should be applicable to the preparation of other polyboron complex cations. However, the ease of hydride abstraction must be dependent upon the hydridic nature of the borane hydrogens on the substrate borane compound. As the borane structure becomes larger, the borane hydrogen atoms are expected to become less hydridic.² Furthermore, the hydridic character of borane hydrogen atoms should be influenced by the number of the trimethylphosphines that are attached to the borane framework. It was, therefore, of interest to test the reaction on other higher borane compounds containing different numbers of trimethylphosphines. Synthesizing new polyboron cations was of interest by itself. In particular, the structures of these cations were of interest. The above tetraboron cation is isoelectronic and isostructural with $B_4H_6-P(CH_3)_3$ and B_4H_5 as $B_4H_6-2P(CH_3)_3^+$, $B_4H_5-P(CH_3)_3$, and B_4H_4 are isoelectronic and isostructural with each other.³ The generality of this isoelectronic isostructural feature had yet to be tested. This paper describes the results of these tests, which were performed on trimethylphosphine adducts of pentaborane(9).

Results and Discussion

A. Reaction of Bis(trimethylphosphine)-Pentaborane(9) with Trityl Cation. The adduct $B_5H_7-2P(CH_3)_3$ reacted with trityl tetrafluoroborate or hexafluorophosphate in dichloromethane at -80 °C to give the $B_5H_7-2P(CH_3)_3^+$ cation. The BF_4^- salt of this cation was reasonably stable at room temperature, but the PF_6^- salt decomposed rapidly above 0 °C.

NMR Spectra. The NMR data for the $B_5H_7-2P(CH_3)_3^+$ cation are listed in Table I. The ^{11}B spectra shown in Figure 1 immediately indicate that the molecule is of C_2 symmetry and that the -49.4 ppm signal is due to the apex boron atom⁴ to which one of the phosphines is attached. The triplet feature of the -14.3 ppm signal (due to the other phosphine-attached boron atom) and the two doublet signals at 0.3 and 6.9 ppm suggest the structure of the cation to be that shown in Figure 1. The assignments were based on the 1H spectra obtained by the selective decoupling of boron spins.

B. Reaction of Trimethylphosphine-Pentaborane(9) with Trityl Cation. A 1:1 mixture of $B_5H_7-P(CH_3)_3$ and trityl tetrafluoroborate in dichloromethane remained unchanged at -80 °C. At -30 °C, however, a rapid reaction occurred and the $B_5H_7-P(CH_3)_3^+$ cation was produced. The BF_4^- salt of this cation was

Table I. NMR Shift Data for the $B_5H_7-2P(CH_3)_3^+$ Cation

| temp, °C | shift in ppm, assign (J in Hz, J_{XY}) [rel intens] |
|--------------|--|
| ^{11}B +20 | -49.4, B_1 (143, J_{BP}) [1]; -14.3, B_2 (103, J_{BP}) [1]; -9.7, B_3 [1]; +0.3, B_4 (125, J_{BH}) [1]; 6.9, B_5 (128, J_{BH}) [1] |
| 1H -10 | 1.84, $H_{B_1CH_3}$ [1]; -1.21, $H_{B_2CH_3}$ [1]; -0.75, $H_{B_3CH_3}$ [1]; 1.87, H_2 [1]; 1.93, H_3 [1]; 2.44, H_4 [1]; 3.21, H_5 [1]; 3.46, H_6 [1]; 1.36, H_{C1H} (11.9, J_{HP}) [9]; 1.56, H_{C2H} (12.8, J_{HP}) [9] |
| ^{31}P +20 | 2.3, P_1 (146, J_{PB}) [1]; -5.3, P_2 [1] |

Table II. NMR Shift Data for the $B_5H_6-P(CH_3)_3^+$ Cation

| temp, °C | shift in ppm, assign (J in Hz, J_{XY}) [rel intens] |
|-------------|--|
| ^{11}B 20 | -48.6, B_1 (220, J_{BP}) [1]; -11.2, B_2 (145, J_{BH}) [4] |
| 1H -10 | 1.54, H_6 [4]; 2.86, H_1 (168, J_{HB}) [4]; 1.74, H_2 (13, J_{HP} , 3, J_{PB}) [9] |
| ^{31}P 10 | 9.5 (215, J_{PB}) |

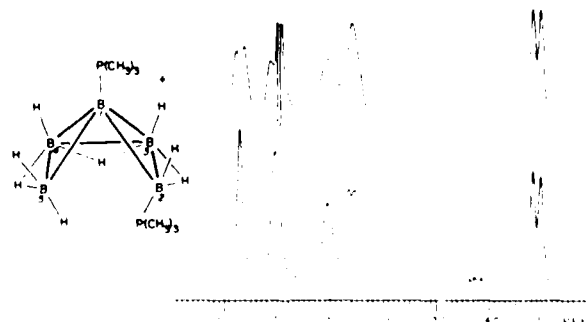


Figure 1. Left, Structure proposed for $B_5H_7-2P(CH_3)_3^+$. Right, 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, +20 °C, CD_2Cl_2 solvent). The upper spectrum is normal, the lower spectrum is proton spin decoupled. The truncated tall peak at -0.4 ppm is due to BF_4^- .

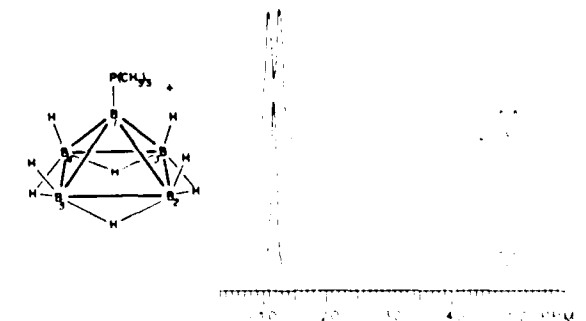


Figure 2. Left, Structure proposed for $B_5H_6-P(CH_3)_3^+$. Right, 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, 20 °C, CD_2Cl_2 solvent). The upper spectrum is normal, the lower spectrum is proton spin decoupled.

fairly stable at room temperature. When trityl hexafluorophosphate was used, the pentaboron cation could not be obtained. Apparently, the PF_6^- ion was involved in the reaction. Thus, even at -80 °C $B_5H_7-P(CH_3)_3$ was consumed and various boron compounds were produced. These compounds included BF_4^- , $BF_3-P(CH_3)_3$, B_5H_6 , $BH_3-P(CH_3)_3$, and other unidentified species.

NMR Spectra. The data are listed in Table II. The ^{11}B spectra shown in Figure 2 suggest that the molecule is of C_4 symmetry. The spectral data are consistent with the structure illustrated in

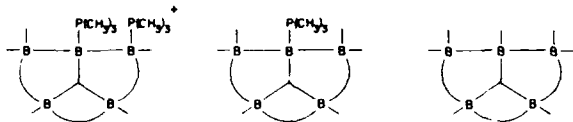
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Figure 2. The extremely large value of J_{BP} (220 Hz) is noteworthy.

C. Pentaborane(9) and Trityl Tetrafluoroborate. Pentaborane(9) did not react with trityl tetrafluoroborate in dichloromethane at room temperature.

D. Conclusion. The reactions described above demonstrated that the attachment of electron-donating trimethylphosphine to pentaborane enhances the hydridic behavior of the borane hydrogen atoms. The ease of hydride abstraction by the trityl cation increases with the number of trimethylphosphines attached to pentaborane.

The new polyboron complex cation $B_5H_9 \cdot 2P(CH_3)_3^+$ is isostructural with its isoelectronic, neutral and anionic counterparts $B_5H_9 \cdot P(CH_3)_3^{\delta+}$ and $B_5H_{10}^{2-}$.



Thus, the isoelectronic-isostructural feature observed for the triboron and tetraboron trios is now extended to the pentaboron trio. It is noted that, among $B_5H_9 \cdot 2P(CH_3)_3^+$, $B_5H_9 \cdot P(CH_3)_3$, and $B_5H_{10}^{2-}$, the anion is most fluxional with respect to its borane hydrogen atom migration^{6,7} and the cation is least fluxional. The same trend has been observed for the corresponding trios of tri- and tetraboron.^{1,3} The other new cation, $B_5H_9 \cdot P(CH_3)_3^+$, belongs to a new family of polyboron complex cations with the general formula $B_nH_{n+2} \cdot P(CH_3)_3^+$, and it is isostructural also with its isoelectronic, neutral counterpart B_nH_n .

Two different salts of the trityl cation were used in this study. The BF_4^- salt yielded reasonably stable salts of the pentaboron cations, but the PF_6^- salt did not. Whenever the PF_6^- salt was used, BF_4^- and $BF_4^- \cdot P(CH_3)_3$ were formed. The interaction of the PF_6^- ion with borane species is an interesting subject of a separate study, and the results will be reported at a later date upon completion of the study.

Experimental Section

General Information. Conventional vacuum-line techniques were used throughout for the handling of air-sensitive, volatile compounds. Nitrogen gas filled, plastic bags were used for the transfer of air-sensitive solids. Pentaborane(9) (Callery Chemical Co.) was fractionated and treated with trimethylphosphine (laboratory stock, prepared by a literature method⁸) to prepare the samples of $B_5H_9 \cdot 2P(CH_3)_3^+$. The sample of $B_5H_9 \cdot P(CH_3)_3$ was prepared from B_5H_9 and $B_5H_9 \cdot 2P(CH_3)_3$ by the method described previously.⁹ The BF_4^- and PF_6^- salts of the trityl cation (Aldrich Chemical Co. and Alfa Products) were recrystallized from dichloromethane. The NMR spectra were recorded on a Varian XL-100 or XL-300 spectrometer. Chemical shifts for ^{11}B and ^{31}P resonances were recorded with reference to the $BF_3 \cdot O(C_2H_5)_2$ and 85% orthophosphoric acid signals, respectively. For 1H resonances, the shift of dichloromethane was taken to be at 5.28 ppm. The reactions of the pentaborane compounds with the trityl salts were performed in 10-mm o.d. Pyrex tubes. The tubes containing reaction mixtures were placed in the probe of the NMR instrument to monitor the reactions.

Reaction of $B_5H_9 \cdot 2P(CH_3)_3$ with Trityl Cation. A 0.49-mmol sample of $B_5H_9 \cdot 2P(CH_3)_3$ was dissolved in about 2 mL of CH_2Cl_2 in the reaction tube, and a 0.61-mmol sample of $C(C_6H_5)_3^+BF_4^-$ was added in the tube

above the frozen solution. As the reaction mixture was agitated by shaking the tube in a $-80^\circ C$ bath, the dark yellow color of the trityl cation changed rapidly to a faint yellow. At this stage the original $B_5H_9 \cdot 2P(CH_3)_3$ had been completely converted into the $B_5H_9 \cdot 2P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, a clear, straw yellow solution resulted. At this point the solution did not contain any boron compound other than the BF_4^- salt of the pentaboron cation. The volatile components were evaporated under vacuum, and the resulting pale yellow residue was washed with toluene and then leached with CH_2Cl_2 . By evaporation of the solvent from the leachate, a white solid of the $B_5H_9 \cdot 2P(CH_3)_3^+BF_4^-$ salt was obtained. The solid was contaminated slightly with small amounts of decomposition products, which were produced during the isolation process. The reaction with $C(C_6H_5)_3^+PF_6^-$ (1:1 molar ratio, 0.46 mmol of each reactant) proceeded similarly. However, the formation of BF_4^- was observed at higher temperatures (about $-20^\circ C$) and was fast above $0^\circ C$.

Reaction of $B_5H_9 \cdot P(CH_3)_3$ with Trityl Cation. A 0.59-mmol sample of $B_5H_9 \cdot P(CH_3)_3$ and 0.64 mmol of $C(C_6H_5)_3^+BF_4^-$ were mixed in about 2 mL of CH_2Cl_2 in a reaction tube. At $-80^\circ C$ most of the trityl salt remained undissolved, and the solution was dark yellow. When the mixture was allowed to warm to $-50^\circ C$ and agitated by shaking, the trityl salt quickly disappeared and the solution became pale yellow and turbid. At this point $B_5H_9 \cdot P(CH_3)_3$ had been converted into the $B_5H_9 \cdot P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, the solution became clear. To isolate the $B_5H_9 \cdot P(CH_3)_3^+BF_4^-$ salt, this solution was treated in the same manner as the $B_5H_9 \cdot 2P(CH_3)_3^+$ cation solution. (See above.) During this isolation process, however, a small portion of the salt decomposed; thus, the product was contaminated. It was noted that as the salt was freed from triphenylmethane, its solubility in CH_2Cl_2 decreased markedly.

Mixtures of B_5H_9 and Trityl Salt. Approximately 0.84-mmol samples of $C(C_6H_5)_3^+BF_4^-$ were mixed with B_5H_9 in 1:2 and 2:1 molar ratios in 2-mL portions of CH_2Cl_2 . When allowed to warm to room temperature, the reaction mixtures were dark brownish yellow. The ^{11}B NMR spectra of these solutions contained only the signals of B_5H_9 and BF_4^- and were found to be unchanged when examined 2 days later.

Acknowledgment. We acknowledge support of this work by the U.S. Army Research Office through Grant DAAG-29-85-K-0034.

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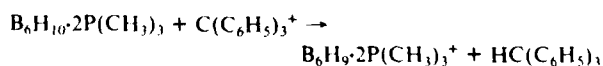
**Formation and Structure of the
Bis(trimethylphosphine)nonahydrohexaboron(1+) Cation**

Mitsuaki Kameda and Goji Kodama*

Received May 19, 1987

Earlier, we reported a series of polyboron complex cations with the formula $B_nH_{n+3} \cdot 2P(CH_3)_3^+$, where $n = 3, 4$, and 5 .¹⁻³ These cations are isostructural with their respective isoelectronic neutral and anionic species as illustrated in Figure 1. The next higher cation of series is $B_6H_9 \cdot 2P(CH_3)_3^+$, and its corresponding isoelectronic species are $B_6H_{10} \cdot P(CH_3)_3$ and $B_6H_{11}^-$, which are known to have the boron cluster geometry indicated in Figure 2a.^{4,5} Abstraction of a hydride ion from $B_4H_8 \cdot 2P(CH_3)_3$ and $B_5H_9 \cdot 2P(CH_3)_3$ were the methods for preparing the above tetraboron and pentaboron complex cations, and the structures of these cations could readily be related with those of the parent bis(phosphine) adducts.^{2,3}

The hexaboron cation would be obtainable likewise by abstracting a hydride ion from $B_6H_{10} \cdot 2P(CH_3)_3$.



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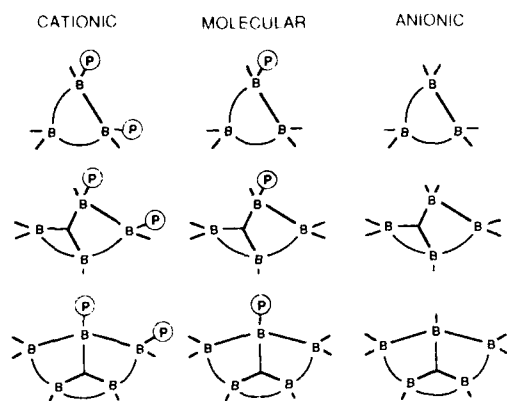


Figure 1. Structures of $B_nH_{n+2}P(CH_3)_3^+$, $B_nH_{n+4}P(CH_3)_3$, and $B_nH_{n+6}P(CH_3)_3^-$ for $n = 3, 4$, and 5 . Hydrogen atoms are not drawn in for brevity. The circled P represents $P(CH_3)_3$.

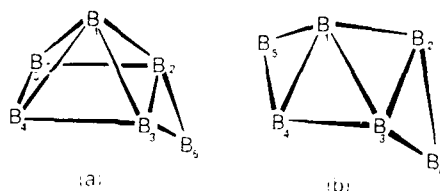


Figure 2. Boron cluster geometry (a) in $B_6H_{10}P(CH_3)_3^+$ and B_6H_{11} and (b) $B_6H_{10}P(CH_3)_3$.

Table I. NMR Data for the $B_6H_9P(CH_3)_3^+$ Cation^a

| ¹¹ B | H | ³¹ P |
|--|-------------------|---------------------------|
| 52.0, t, B(1), $J_{BP} = 214$ | -2.68, H(μ) | 5.7, P(1), $J_{PB} = 214$ |
| 45.0, q, B(6), $J_{BP} = 94$, $J_{BH} = 93$ | 1.05, H(μ) | 2.3, P(6), $J_{PB} = 100$ |
| 20.3, d, B(3,4), $J_{BH} = 150$ | 1.45, H(C H(1)) | |
| 8.9, d, B(2,5), $J_{BH} = 150$ | 1.64, H(C H(6)) | |
| | 2.40, H(3,4) | |
| | 2.94, H(2,5) | |

^aShifts in ppm; J values in Hz. References for the shifts: ¹¹B, $BF_3 \cdot O(C_2H_5)_2$; ³¹P, 85% orthophosphoric acid; ¹H, $\delta(CH_2Cl_2) = 5.28$ ppm. Key: d, doublet; q, quartet. Solvents: CH_2Cl_2 for ¹¹B; CD_2Cl_2 for ³¹P and ¹H. Temperature: -10 °C.

However, the structure of the bis(phosphine) adduct is belt-shaped as shown in Figure 2b⁹ and is quite different from that in Figure 2a. It was, therefore, of interest to prepare the $B_6H_9P(CH_3)_3^+$ cation and to investigate its structure. The results of the study are described in this paper.

Results

The bis(trimethylphosphine) adduct of B_6H_{10} reacted slowly with the trityl cation (BF_4^- or PF_6^- salt) in a 1:1 molar ratio in dichloromethane at -80 °C, and the hexaboron complex cation $B_6H_9P(CH_3)_3^+$ was formed. The BF_4^- salt of the cation slowly decomposed in the solution at room temperature. The PF_6^- salt was less stable, and underwent a rapid decomposition at 0 °C with concomitant formation of BF_4^- . Furthermore, the cation thus produced appeared to slowly undergo certain reactions with the starting compound, producing small amounts of side products. However, the cation could be characterized by NMR spectroscopy, and was found to have a structure similar to that of $B_6H_{10}P(CH_3)_3$ or B_6H_{11} , the phosphines being attached at the apex and bridge boron atoms. See part B of the Discussion.

Discussion

A. Ease of Hydride Abstraction. The above hydride abstraction reaction of $B_6H_{10}P(CH_3)_3$ was slow when compared with those of $B_6H_9P(CH_3)_3$ and $B_6H_8P(CH_3)_3$, which were instantaneous at -80 °C.^{2,3} The increased acidity, or the diminished hydridic character of borane hydrogens, of the larger borane fragment¹ is thought to be responsible for the slower reaction rate. A similar reactivity variation has been observed for the series of pentaborane compounds B_5H_9 , $B_5H_9P(CH_3)_3$, and $B_5H_9P(CH_3)_3^+$.³

B. Structure of $B_6H_9P(CH_3)_3^+$. The ¹¹B, ¹H, and ³¹P NMR data for the $B_6H_9P(CH_3)_3^+$ cation are summarized in Table I. As illustrated in Figure 3, the ¹¹B spectrum of the cation resembles that of $B_6H_{10}P(CH_3)_3$,⁴ the noticeable differences being that the most shielded signal for the cation is a B-P doublet whereas the corresponding one for $B_6H_{10}P(CH_3)_3$ is a B-H doublet and that each signal of the cation, with the exception of the -45.0 ppm quartet signal (due to the bridging boron, to which the other $P(CH_3)_3$ is attached), is shifted downfield from the corresponding signal of $B_6H_{10}P(CH_3)_3$. The extremely large B-P coupling constant of 212 Hz for the most shielded signal of the hexaboron cation is comparable with the value of 220 Hz that was observed for the apex B-P coupling constant of the square-pyramid-shaped $B_5H_9P(CH_3)_3^+$ cation.³ Compared with the chemical shift of basal boron atoms of B_5H_9 , the corresponding signal of this pentaboron cation is shifted downfield also. Thus, replacement of H by $P(CH_3)_3$ at the apex position of $B_6H_{10}P(CH_3)_3$ results in the structure of $B_6H_9P(CH_3)_3^+$, which is consistent with the ¹¹B NMR data observed for the hexaboron cation. The assignments for the ¹H resonance signals listed in Table I were straightforward with the use of single-frequency decoupling techniques on the ¹¹B spins. The signals of hydrogens on the bridge boron atom could not be located. Probably, the signal is overlapped with the closely spaced, intense two signals of methyl hydrogens.

C. Structure Transformation. The isoelectronic isostructural feature that was observed for the tri-, tetra- and pentaboron trios^{1,2,3} has now been extended to the trio of arachno hexaboron species, $B_6H_9P(CH_3)_3^+$, $B_6H_{10}P(CH_3)_3$, and B_6H_{11} . Addition of a Lewis base, $P(CH_3)_3$, to $B_6H_{10}P(CH_3)_3$ results in a hypothetical hexaborane compound, $B_6H_{10}P(CH_3)_3$.⁴ Through this process the structure changes from the basal-bridged square pyramid to the belt-shaped arrangement of six boron atoms. Conversely, removal of a Lewis base, H, from $B_6H_{10}P(CH_3)_3$ reverts the structure to the basal-bridged square pyramid of *arachno*- $B_6H_9P(CH_3)_3^+$. This transformation scheme is illustrated in Scheme 1. At present, nothing definitive can be stated about the mechanism of transformation. The B-P bonds, because of their considerable strength, would remain undissociated throughout the process of the transformation. Providing that this assumption is correct, the observed final structure may be attained through certain framework isomerizations such as that involving the diamond-square-diamond (dsd)⁹ rearrangements.

Two different boron framework structures are known to be assumed by arachno hexaborane compounds. One is the basal-bridged square pyramid, which is dealt with in this study. The other is the belt-shaped structure of B_6H_{11} ,⁹ which is similar to that of $B_6H_{10}P(CH_3)_3$. As the "skeletal electron counting" formalism dictates,¹⁰ both of these structures can be derived from the eight-vertex deltahedron (bisdisphenoid) by removing two vertices.¹¹ An apparent difference between the two sets of the

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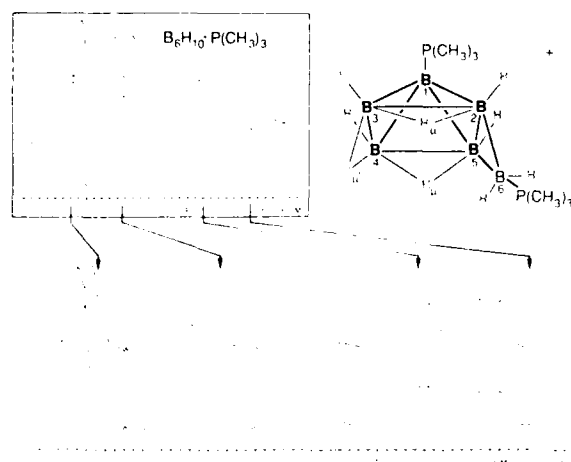


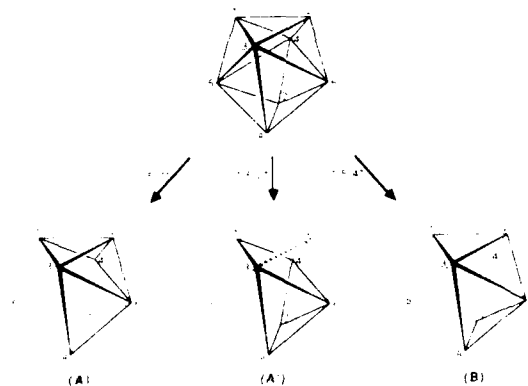
Figure 3. Structure and ^{11}B NMR spectra (96.2 MHz) of $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3^+$. Spectra (32.1 MHz) of $\text{B}_6\text{H}_{10}\text{P}(\text{CH}_3)_3$ are shown in the box for comparison: top, normal spectrum; bottom, proton spin decoupled spectrum.

arachno compounds is in the number of ligands that are associated with six-boron clusters—11 versus 12. Obviously, however, further studies need to be pursued to elucidate the factors that determines the structure of an arachno hexaborane compound.

Experimental Section

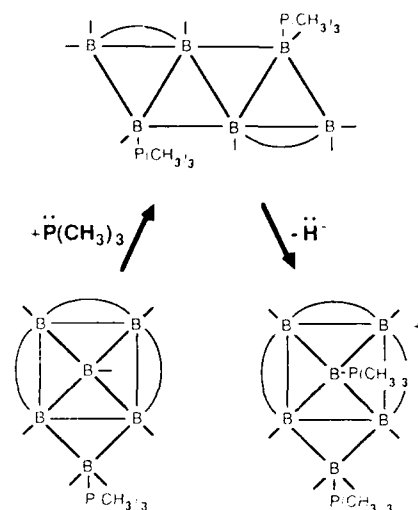
General consideration and procedures for the experiments were the same as those described in the previous reports.^{2,3} The NMR data were

- (11) Examples of the vertex removal to achieve structures a and b are illustrated below. Removal of vertices 5 and then 7 (indicated as "5,7")



results in structure A, which does not have the C_4 symmetry as it is. The resulting framework (A) needs to slightly adjust itself to achieve the structure shown in Figure 2a. Route "5,2" leads to structure A', which is of C_4 symmetry. Choice of the two routes is arbitrary. In the B_6H_{12} ion, the bridging BH_2 group is bonded to the two basal boron atoms via a B-B bond and a B-H-B bond.⁴ In this sense, structure A' may be appropriate for the anion. Whereas, in $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3^+$ and $\text{B}_6\text{H}_{10}\text{-P}(\text{CH}_3)_3$, the two basal boron atoms are bonded by a bridging $\text{BH}_2\text{-P}(\text{CH}_3)_3$ group via a closed BBB three-center bond. Structure A, therefore, may fit better to the description of these two species.

Scheme 1



obtained on a Varian XL-300 NMR spectrometer. Samples of $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$, which had been obtained as the byproduct of $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3$ (or $\text{CH}_3\text{B}_2\text{H}_3\text{-}2\text{P}(\text{CH}_3)_3$) preparation by the reaction of B_6H_6 (or $\text{CH}_3\text{B}_2\text{H}_6$) with excess $\text{P}(\text{CH}_3)_3$,¹² were washed with diethyl ether to remove remaining $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3$ (or $\text{CH}_3\text{B}_2\text{H}_3\text{-}2\text{P}(\text{CH}_3)_3$) and then extracted with dichloromethane. The $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$ sample thus obtained was a free-flowing crystalline solid, and its ^{11}B NMR spectrum indicated that the sample was essentially pure, traces of impurities being $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3$ and unidentified boron compounds. The hydride abstraction reactions were run in 10 mm o.d. Pyrex tubes and were monitored with use of the NMR instrument.

Reaction of $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$ with Trityl Salts. A 0.43-mmol sample of $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$ was mixed with 0.37 mmol of $\text{C}(\text{C}_6\text{H}_5)_3^+\text{PF}_6^-$ in 1.5 mL of dichloromethane at -80°C . The intense dark yellow color of the solution was seen to slowly fade. When $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$ was treated similarly with $\text{C}(\text{C}_6\text{H}_5)_3^+\text{BF}_4^-$ in a 1:2, 1:1, or 2:1 molar ratio, the same slow change occurred also. To ensure the completion of reaction, these solutions were either kept at -80°C for a period of over 50 h or briefly warmed to 0°C . (The system containing the PF_6^- ion slowly produced BF_4^- ion when warmed to -45°C .) The 2:1 reaction mixture gave the final solution containing the original $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$ and the $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3^+$ cation in an approximately 1:1 molar ratio.

Acknowledgment. This work was supported by the U.S. Army Research Office through Grant DAAG29-85-K-0034. The NMR instrument was acquired by the university with use of instrumentation funds provided by the National Science Foundation and the Department of Defense. We gratefully acknowledge these generous supports.

Registry No. $\text{B}_6\text{H}_{10}\text{-}2\text{P}(\text{CH}_3)_3$, 57034-29-4; $\text{C}(\text{C}_6\text{H}_5)_3^+\text{PF}_6^-$, 341-02-6; $\text{C}(\text{C}_6\text{H}_5)_3^+\text{BF}_4^-$, 437-17-2; $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$, 110795-78-3; $\text{B}_6\text{H}_4\text{-}2\text{P}(\text{CH}_3)_3^+\text{PF}_6^-$, 110795-79-4.

- (12) (a) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288. (b) The reaction of $\text{CH}_3\text{B}_2\text{H}_6$ with $\text{P}(\text{CH}_3)_3$. Kameda, M.; Driscoll, J. A.; Kodama, G., unpublished results.

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CHEMISTRY OF LOWER BORANES INVOLVING TRIMETHYLPHOSPHINE

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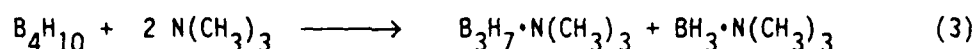
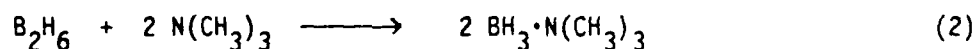
CHEMISTRY OF LOWER BORANES INVOLVING TRIMETHYLPHOSPHINE

1. INTRODUCTION

In 1975, A.R.Dodds clarified the reaction of pentaborane(11) with trimethylamine in this laboratory,¹

$B_5H_{11} + 2 N(CH_3)_3$ (used in excess) $\longrightarrow B_4H_8 \cdot N(CH_3)_3 + BH_3 \cdot N(CH_3)_3$ (1)
 and isolated the trimethylamine adduct of tetraborane(8) as a sublimable solid at room temperature. This finding had a strong impact and a significant influence on the subsequent development of the reaction chemistry of smaller boranes that involved strong Lewis bases.

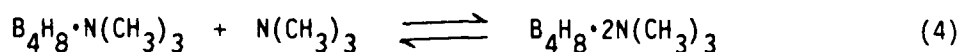
Trimethylamine was known to cleave diborane(6)² and tetraborane(10)³ to give the trimethylamine adducts of boranes:



It therefore was referred to as one of the typical Lewis bases that effected "symmetrical cleavage" of boranes. [The term "symmetrical cleavage" is used for a type of borane cleavage reactions that produces a BH_3 fragment, e.g., equations 1, 2, and 3. For another type of borane cleavage that produces a BH_2^+ unit, the term "unsymmetrical cleavage" is used.^{4,5} Typical examples of the unsymmetrical cleavage are seen in the reactions of B_2H_6 , B_4H_{10} , and B_5H_{11} with ammonia, which give the BH_4^- , $B_3H_8^-$, and $B_4H_9^-$ salts of the $H_2B(NH_3)_2^+$ cation, respectively^{4,6,7}]. However, the reaction of this base with pentaborane(11) did not appear to give the expected symmetrical

cleavage products of pentaborane(11), $B_4H_8 \cdot N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3$. reported⁸ that the reaction gave a complex mixture of boron hydride compounds. This observation was reproducible also in this laboratory in earlier days. On the other hand, the symmetrical cleavage of pentaborane(11) with CO^9 and PF_2X [$X = F,^{10} Cl,^{10} Br,^{10} I,^{10} H,^{11}$ and $N(CH_3)_2^{11,12}$] had been established, and the B_4H_8 adducts of these Lewis bases had been isolated and characterized. It was generally assumed, on the basis of these observations, that " $B_4H_8 \cdot N(CH_3)_3$ " was unstable due to the strong basicity of trimethylamine.^{5,8b}

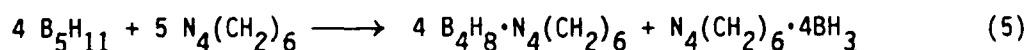
Dodds initially prepared $B_4H_8 \cdot N(CH_3)_3$ by adding trimethylamine to a mixture of $BH_3 \cdot S(CH_3)_2$ and $B_4H_8 \cdot S(CH_3)_2$,¹³ which was obtained from the reaction of pentaborane(11) with dimethylsulfide. Once isolated, $B_4H_8 \cdot N(CH_3)_3$ was found to be stable toward Lewis bases. In the presence of excess trimethylamine, the integrity of the B_4H_8 unit was maintained and the bis(trimethylamine) adduct of B_4H_8 was formed. The bis(amine) adduct could be isolated below $-40^\circ C$.



These trimethylamine adducts of B_4H_8 , however, were very reactive to acids including pentaborane(11). It was this property of the adducts that caused the difficulty in isolating $B_4H_8 \cdot N(CH_3)_3$ in earlier days. When pentaborane(11) and trimethylamine were mixed in a 1:2 molar ratio and the reaction was allowed to proceed slowly at low temperatures, a portion of the initially formed $B_4H_8 \cdot N(CH_3)_3$ reacted with pentaborane(11) which was still present, and thus the reaction mixture was contaminated with unstable side products. Isolation of the B_4H_8 adduct from such a mixture became extremely

difficult if not impossible. The unfavorable secondary reactions were suppressed and the symmetrical cleavage reaction of the borane was effected cleanly by using an excess of trimethylamine in the cleavage reaction of B_5H_{11} (equation 1).

H.Kondo in this laboratory prepared the hexamethylenetetramine adduct of B_4H_8 by the following reaction in chloroform.¹⁴

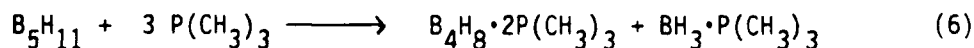


The observed thermal stability of these amine adducts of B_4H_8 was, contrary to the earlier speculation, not lower than that of the other previously reported adducts of B_4H_8 , and was certainly higher than that of the weakly basic CO or PF_3 adduct. The above observations taken together prompted the investigation of related borane chemistry in which strong bases were involved. Trimethylphosphine was chosen as the base to be tested for the investigation because of its established strong base character toward boranes,¹⁵ the absence of detrimental functional groups attached to it, and the ease of its handling in conventional vacuum lines.

2. REACTIONS OF SOME BORANES WITH EXCESS TRIMETHYLPHOSPHINE

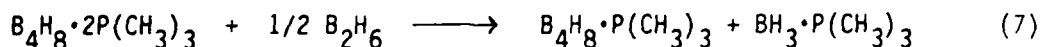
2.1. Pentaborane(11)

When treated with excess trimethylphosphine, pentaborane(11) was cleaved cleanly into the B_4H_8 and BH_3 fragments.¹⁶



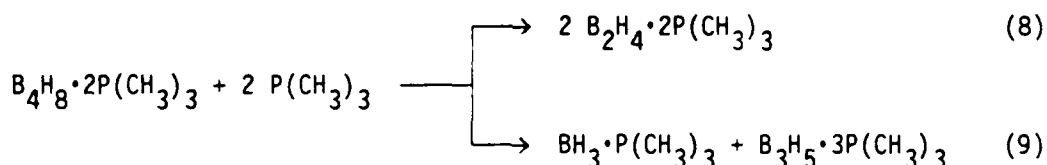
Unlike the bis(amine) adduct, the bis(phosphine) adduct would not dissociate at room temperature. Because of the stability of this adduct, preparation of

the mono-adduct $B_4H_8 \cdot P(CH_3)_3$ was better accomplished by treating the bis(adduct) with diborane¹⁷:

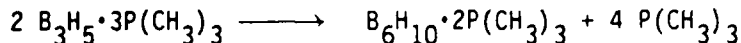


Several other indirect methods were developed for the preparation of $B_4H_8 \cdot P(CH_3)_3$ and were summarized in a separate paper.¹⁷ The reaction of pentaborane(11) with trimethylphosphine in a 1:2 molar ratio gave an unfavorable result similar to what was observed in the reaction with trimethylamine. The mono(trimethylphosphine) adduct of B_4H_8 was a sublimable solid and was more stable than the corresponding trimethylamine adduct. Apparently, the strong basicity of trimethylphosphine provided a strong bond between the borane fragment and the base, and thus increased the stability of the adduct.

When $B_4H_8 \cdot 2P(CH_3)_3$ was treated with excess trimethylphosphine, two different modes of cleavage reaction slowly occurred according to the following equations.¹⁸

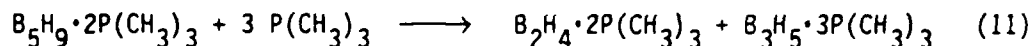


The distribution of the two cleavage modes appeared to depend upon the reaction conditions. The cleavage products were stable at room temperature in the presence of excess $P(CH_3)_3$ and did not undergo further changes. Although $BH_3 \cdot P(CH_3)_3$ and $B_2H_4 \cdot 2P(CH_3)_3$ are sublimable solids at room temperature, the triborane adduct is unstable. It released two of its three phosphines when subjected to pumping above 0°C, and changed into the bis(trimethylphosphine) adduct of hexaborane(10)¹⁹:



2.2. Pentaborane(9)

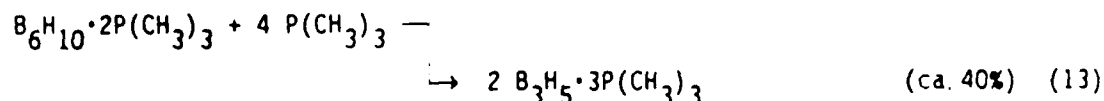
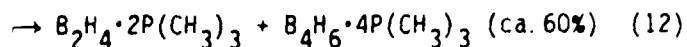
When pentaborane(9) was treated with a large excess of trimethylphosphine in acetonitrile or dichloromethane, or when it was dissolved in trimethylphosphine, $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$ which formed initially,¹⁷ reacted slowly with the phosphine at room temperature and a colorless, clear solution resulted. One of the products was $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ and, contrary to the general expectation at that time, no $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ was formed. On the basis of the observed reaction stoichiometry, the yield of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ and the result of the vapor pressure depression measurements of trimethylphosphine solutions of the products, the reaction was represented by the following equation¹⁹:



This reaction represented a new type of borane cleavage, a cleavage that did not produce a BH_3 adduct.

2.3. Hexaborane(10)

Hexaborane(10) also underwent cleavage reactions when treated with a large excess of trimethylphosphine. This reaction was preceded by the stepwise formation of $\text{B}_6\text{H}_{10} \cdot \text{P}(\text{CH}_3)_3$ ²¹ and $\text{B}_6\text{H}_{10} \cdot 2\text{P}(\text{CH}_3)_3$.²² The cleavage appeared to occur in two different modes as indicated below.²³



The results were similar to those observed for B_5H_9 : Formation of $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ did not occur, the resulting solution in liquid trimethylphosphine remained colorless and clear for days at room temperature, and the final products were all "electron sufficient" (or electron precise).

The above described reactions of boranes with excess trimethylphosphine demonstrated that treatment of boranes with a strong base does not necessarily result in the formation of an intractable mixture of borane compounds. Generally, the resulting borane adducts are reactive towards acids, but are inert to bases. The ultimate "inertness" of the borane adducts toward bases is reached when electron sufficiency is attained. This is achieved by removal of electron deficiency by successive base additions. Strong bases are more capable than weaker bases of removing the "electron deficiency" from borane compounds. Cleavage of the borane framework occurs during this process of base addition. [Nido boranes (e.g. B_5H_9 and B_6H_{10}) are cleaved into two fragments, and arachno boranes (e.g. B_4H_{10} and B_5H_{11}) are cleaved into three fragments.] Ultimately, each mole of pentaborane(9) and pentaborane(11) reacted with five moles of $\text{P}(\text{CH}_3)_3$ and each mole of hexaborane(10) reacted with six moles of $\text{P}(\text{CH}_3)_3$, to produce the electron sufficient adducts of borane fragments.

3. THE HYPHO CLASS ADDUCTS OF TETRABORANE(8)

3.1. Formation of $B_4H_8 \cdot L \cdot L'$

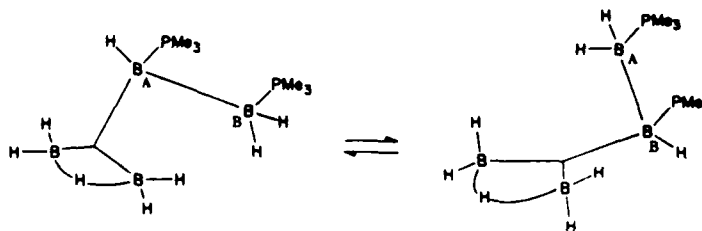
The bis(trimethylamine) and bis(trimethylphosphine) adducts of tetraborane(8) both belong to the hypho class of boron hydride compounds. At the time these two compounds were isolated only a few hypho class tetraborane adducts were known. Muetterties²⁴ obtained $B_4H_8 \cdot TMED$ (TMED = tetramethylethylenediamine) by the alcoholysis of $B_5H_9 \cdot TMED$ which he obtained by the direct reaction of B_5H_9 with the diamine. The two unstable adducts of carbon monoxide-tetraborane(8), $B_4H_8 \cdot CO \cdot (CH_3)_2O$ and $B_4H_8 \cdot CO \cdot CH_3CN$, which were reported by Burg,²⁵ may also be classified as hypho adducts of B_4H_8 . Formation of the $N(CH_3)_3$ and $P(CH_3)_3$ adducts of $B_4H_8 \cdot CO$ was observed as unstable intermediates in the carbon monoxide displacement reactions of $B_4H_8 \cdot CO$ with these bases.²⁶

In general, both $B_4H_8 \cdot N(CH_3)_3$ and $B_4H_8 \cdot P(CH_3)_3$ reacted with various Lewis bases (L) of adequate strength to form hypho class adducts with the formulas $B_4H_8 \cdot N(CH_3)_3 \cdot L$ ¹ and $B_4H_8 \cdot P(CH_3)_3 \cdot L$.¹⁷ Furthermore, even the nonahydrotetraborate(1-) anion ($B_4H_9^-$), which may formally be considered to be the H^- adduct of B_4H_8 , combined with some Lewis bases to give anionic adducts ($B_4H_9 \cdot L^-$).²⁷ These bis(base) adducts prepared in this laboratory are $B_4H_8 \cdot 2N(CH_3)_3$,^{1c} $B_4H_8 \cdot N(CH_3)_3 \cdot N(CH_3)_2H$,^{1c} $B_4H_8 \cdot N(CH_3)_3 \cdot N(CH_3)H_2$,^{1c} $B_4H_8 \cdot N(CH_3)_3 \cdot NH_3$,^{1c} $B_4H_8 \cdot 2P(CH_3)_3$,¹⁶ $B_4H_8 \cdot P(CH_3)_3 \cdot P[N(CH_3)_2]_3$,¹⁷ $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$,¹⁷ $B_4H_9 \cdot P(CH_3)_3$,²⁷ $B_4H_9 \cdot P[N(CH_3)_2]_3$,¹⁷ and $B_4H_9 \cdot NH_3$.^{27,29} The stability of each of the adducts listed is dependent upon the nature of the ligand bases involved. The bis(trimethylphosphine)

adduct is stable enough to be sublimed at room temperature, but the other adducts can be isolated or identified only at low temperatures. At higher temperatures, these unstable adducts either lose the weaker of the two bases, or undergo complex decompositions.

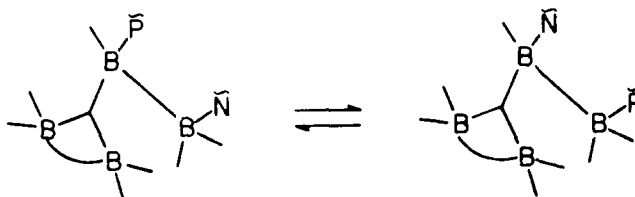
3.2. Site Preference of the Two Different Bases

One of the characteristic properties common to the bis(base) adducts of B_4H_8 is the fluxional behavior of the molecules. The ^{11}B NMR spectra of $B_4H_8 \cdot 2P(CH_3)_3$ indicated that the molecules were undergoing rapid intramolecular conversions at room temperature.¹⁶



The 1H NMR spectra showed that this conversion was accompanied by rapid migration of all eight hydrogen atoms in the B_4H_8 moiety. In a low temperature ^{11}B spectrum, the signal of the phosphine-attached boron atoms is split (see Figure 1), indicating slowing of the motion at that temperature. By comparing the two shift values of the phosphine-attached boron atoms with those of $B_3H_7 \cdot P(CH_3)_3$ and $BH_3 \cdot P(CH_3)_3$, the high-field and low-field signals were assigned to the apical and basal boron atoms, respectively. Presumably, a similar conversion occurs in $B_4H_8 \cdot 2N(CH_3)_3$ molecules.

In the hetero-bis(base) adducts, this type of rapid conversion brings about an equilibrium of two isomers. The site preference of the two different bases determines the relative stabilities of the two isomers. An example is seen in $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$.¹⁷ At $-30^\circ C$, this adduct undergoes a rapid conversion relative to the NMR time scale:



In the ^{11}B NMR spectrum of the compound at $-30^\circ C$, only three signals appear. See Figure 2b. These are assigned to the amine-attached boron atom, the two non-ligated boron atoms and the phosphine-attached boron atom going up-field. At $-80^\circ C$ the phosphine-attached boron signals are split into two. See Figure 2a. The amine-attached boron signal also should be split although this is not apparent in the figure due to the broadness and the overlap of the signals. As in the case of $B_4H_8 \cdot 2P(CH_3)_3$, the more intense, high-field signal of the two phosphine-attached boron signals is assigned to the apex boron atom. Thus, trimethylphosphine prefers the apical position to the basal position in the structure when competing with trimethylamine.

3.3. Another Form of the Diammoniate of Tetraborane(10)

Tetraborane(10) forms an ammoniate with the formula $H_2B(NH_3)_2^+ B_3H_8^-$.⁶ The original preparation of this diammoniate of

tetraborane(10) was performed under a specific set of reaction conditions. Tetraborane(10) and ammonia were mixed in a 1:2 molar ratio in diethyl ether at -78 °C and the mixture was aged for a week at that temperature. Removal of the solvent from the resulting solution gave a crystalline solid of the diammoniate. The formation of the diammoniate of tetraborane(10) was compared with the formation of the diammoniate of diborane(6) $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$,⁴ and was taken as a typical case of the "unsymmetrical" cleavage of tetraborane(10). However, the reason for these particular reaction conditions for the diammoniate formation was not completely understood. If ammonia was added in excess, or if the temperature was raised rapidly above -40 °C, complex reactions occurred, unstable products formed, and the diammoniate could not be obtained.

The adduct formation of the B_4H_9^- anion mentioned earlier in this section offers an explanation for the restricted conditions, when combined with the following observation made by Shore and coworker. They showed²⁸ that tetraborane(10) undergoes a rapid, reversible deprotonation reaction with ammonia ($\text{B}_4\text{H}_{10} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+\text{B}_4\text{H}_9^-$), and that the irreversible cleavage reaction proceeds slowly to give $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{B}_3\text{H}_8^-$. If ammonia is present in excess and in high concentration, it will react with the initially produced B_4H_9^- to give the $\text{B}_4\text{H}_9\cdot\text{NH}_3^-$ anion. The adduct anion is stable only below -40 °C and, unlike the B_4H_9^- anion, it will not revert to B_4H_{10} . Thus, the presence of the adduct anion renders the entire product of the reaction unstable and intractable. The formation of this anion could be minimized by using solvent, by keeping the temperature low and by limiting the amount of ammonia in the reaction mixture.

The ^{11}B NMR spectrum of a liquid ammonia solution of tetraborane(10) (below -45°C) was identical with that of an ammonia solution of KB_4H_9 , indicating the exclusive formation of $\text{NH}_4^+\text{B}_4\text{H}_9\cdot\text{NH}_3^-$.²⁹ This ammonium salt has the composition " $\text{B}_4\text{H}_{10}\cdot 2\text{NH}_3$ ", and thus represents another form of the diammoniate of tetraborane(10). Furthermore, the formation of such an adduct anion may help to explain, at least in part, the even more stringent reaction conditions that were required for the preparation of the diammoniate of pentaborane(11), $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{B}_4\text{H}_9^-$.⁷

4. REACTION CHEMISTRY OF $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$

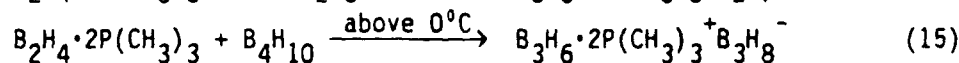
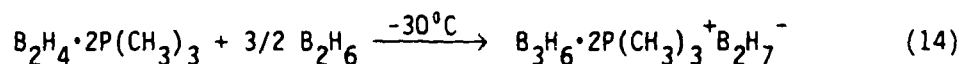
In an earlier section, the formation of "electron sufficient" borane adducts was described. A boron hydride compound with the formula $\text{B}_n\text{H}_{2n+2}^{n-}$ is electron sufficient (or electron precise), and the molecule is of chain structure. The number of skeletal electrons³⁰ for such a molecule is $4n + 2$, or $2n + (2n + 2)$. Replacement of n number of H^- in such a molecule by the same number of trimethylphosphine gives a neutral trimethylphosphine adduct which is electron sufficient. These molecular adducts are represented by the following series of adducts: $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$, $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$, $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$, $\text{B}_4\text{H}_6\cdot 4\text{P}(\text{CH}_3)_3$ and so forth.

Each member of the above series, because of its electron sufficiency and because of the strong donor property of the trimethylphosphine in it, was expected to be more susceptible to electrophilic reagents and to have its borane hydrogen atoms more hydridic in character, than other neutral boranes

and borane adducts which contain the same number of boron atoms but fewer skeletal electrons. Thus, these adducts were expected to show certain behaviors characteristic of bases. It was of interest to investigate the reaction chemistry of $B_2H_4 \cdot 2P(CH_3)_3$ to reveal the properties of the adduct that stem from its electron sufficiency.

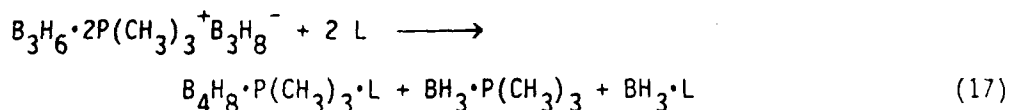
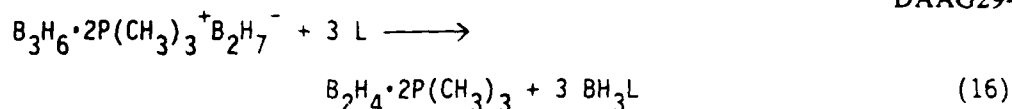
4.1. Formation of the $B_3H_6 \cdot 2P(CH_3)_3^+$ Cation

Bis(trimethylphosphine)diborane(4), $B_2H_4 \cdot 2P(CH_3)_3$, reacted with diborane(6) and with tetraborane(10) according to the following equations.³¹



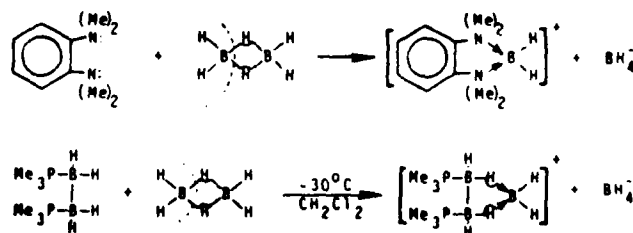
Although the $B_2H_7^-$ salt of bis(trimethylphosphine)hexahydrotriboron(1+) cation was stable only below $-30^\circ C$, the $B_3H_8^-$ salt was stable at room temperature. The structure of $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$ ³² is shown in Figure 3. The cation is isoelectronic and isostructural with $B_3H_7 \cdot P(CH_3)_3$ and $B_3H_8^-$. Successive replacement of trimethylphosphine in the cation by H^- yields the structures of the neutral and anionic compounds.

The triboron complex cation is stable toward acids but reactive toward bases. Thus, the reaction of the $B_2H_7^-$ salt with anhydrous HCl gives the HCl_2^- salt,³¹ and with HCl in the presence of BCl_3 gives the BCl_4^- salt of the cation.³³ With trimethylamine or trimethylphosphine, however, the cation undergoes reactions, which apparently are dependent upon the nature of the counter anions. For example,³⁴

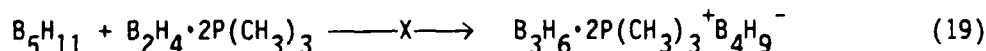
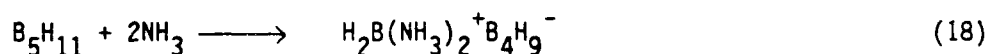


where $\text{L} = \text{N}(\text{CH}_3)_3$ or $\text{P}(\text{CH}_3)_3$.

Earlier, Parry and Edwards⁵ extended their coordination chemistry view of boron hydride compounds such as $\text{H}_2\text{B}(\text{NH}_3)_2^+$ and $\text{H}_3\text{B} \cdot \text{NH}_3$, to the formation of B-H-B bridge bonds, and considered the bridge bond formation as a result of the coordination of the B-H hydrogen to the other boron atom. The scheme may be represented as $\text{B}-\text{H} \rightarrow \text{B}$. A number of boron hydride compounds can be regarded, by this formalism, as coordination compounds containing the $\text{B}-\text{H} \rightarrow \text{B}$ coordinate bonds. For example, tetraborane(10) can be regarded as a coordination compound resulting from the combination of BH_3 and B_3H_7 groups, each of the two groups serving as both an acid and a base, or can be regarded as the result of chelate coordination of B_3H_8^- to BH_2^+ . In this Parry-Edward's view, the above described triboron cation may be looked upon as a complex of BH_2^+ with a bidentate ligand $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ coordinating through two B-H-B bridge bonds. Thus, the formation of the triboron cation from diborane(6) and tetraborane(10) compares with the reactions of these boranes with diamines, in which chelate complex cations are formed.^{35,36}



In terms of the borane cleavage classification, the above formation of the triboron cation is the unsymmetrical cleavage of diborane(6) and tetraborane(10) by a base, $B_2H_4 \cdot 2P(CH_3)_3$. Certain bases bring about the unsymmetrical cleavage of both diborane(6) and tetraborane(10). Some of these bases, such as ammonia, also cause unsymmetrical cleavage of pentaborane(11).^{4,6,7} The reaction of $B_2H_4 \cdot 2P(CH_3)_3$ with pentaborane(11), however, did not give the unsymmetrical cleavage products of the borane.



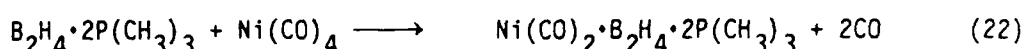
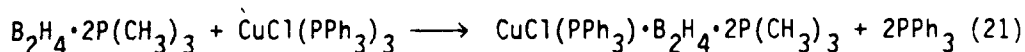
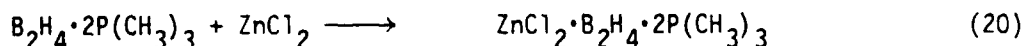
Instead, $B_5H_9 \cdot P(CH_3)_3$ was produced in this reaction which will be described in Section 4.3.

It is noted that bis(trimethylphosphine)-methyldiborane(4) $CH_3B_2H_3 \cdot 2P(CH_3)_3$ gave methyl derivatives of the triboron cation $CH_3B_3H_5 \cdot 2P(CH_3)_3^+$ when treated with diborane(6) or tetraborane(10) (two isomers of the cation were identified),^{31,37} and that the reaction of $B_2H_4 \cdot 2P(CH_3)_3$ with boron trifluoride gave a difluoro derivative of the triboron cation $B_3H_4F_2 \cdot 2P(CH_3)_3^+$ as the $B_2F_7^-$ salt.^{31,37} Thus, the formation of the triboron cation, or the chelation of diborane(4) moieties through two vicinal hydrogen atoms, appears to be a general type of reaction.

4.2. Formation of Metal Complexes of $B_2H_4 \cdot 2P(CH_3)_3$

By extending the coordination chemistry formalism of the triboron cation to systems which contain metals as the coordination center,

$B_2H_4 \cdot 2P(CH_3)_3$ complexes of $ZnCl_2$,³⁸ $CuCl(PPh_3)_3$,³⁸ and $Ni(CO)_2$ ³⁹ were prepared by the following reactions and were isolated at room temperature as solids.



The structure of the zinc complex was confirmed by x-ray method to be similar to that of the triboron complex cation.³⁸ See Figure 4. The infrared and NMR data of these complexes suggested that the structures of the other two metal complexes were similar to that of the zinc compound. These complexes liberated $B_2H_4 \cdot 2P(CH_3)_3$ readily when treated with trimethylphosphine. In the case of the nickel complex, even a weakly basic ligand such as CO, PF_3 , or PH_3 displaced the borane-adduct ligand.³⁹ Anhydrous hydrogen chloride reacted with these complexes and produced the trimethylphosphine adducts of BH_3 and BH_2Cl , which are known to be the cleavage products of $B_2H_4 \cdot 2P(CH_3)_3$ by HCl.¹⁹ The labile nature of the zinc complex was shown in the ^{11}B NMR spectra of a dichloromethane solution containing the complex and excess $B_2H_4 \cdot 2P(CH_3)_3$: The signals of the two compounds coalesced at room temperature.⁴⁰

Examples of the coordination of boron hydride compounds through B-H-M three center bonds are abundant in the literatures.⁴¹ The following are a few of the representative cases: $M(BH_4)_n$ (M = variety of metals, BH_4^- as bidentate or tridentate ligand); $Mn_3(CO)_{10}HB_2H_6$ ($B_2H_6^{2-}$ as bidentate ligand); $Cr(CO)_4B_3H_8^-$ and $Mn(CO)_4B_3H_8$ ($B_3H_8^-$ as bidentate ligand); $Mn(CO)_3B_3H_8$ ($B_3H_8^-$ as tridentate ligand). However, in these compounds the borane ligands are anionic species. Thus, the above described $B_2H_4 \cdot 2P(CH_3)_3$ complexes

demonstrate the ability of a neutral borane adduct to coordinate to metal centers.

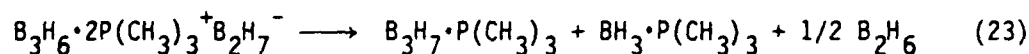
In contrast to the ready complex formation of $B_2H_4 \cdot 2P(CH_3)_3$ with metals, both $BH_3 \cdot P(CH_3)_3$ and $B_3H_7 \cdot P(CH_3)_3$ failed to react with zinc chloride under conditions comparable to those employed for the formation of $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)_3$.⁴⁰ It appears that the observed stability of $B_2H_4 \cdot 2P(CH_3)_3$ complexes is due both to the favorable chelate "bite" distance between the two vicinal hydrogen atoms and to the enhanced hydridic character of the hydrogen atoms in the electron sufficient adduct. In $BH_3 \cdot P(CH_3)_3$ the geminal $H \cdots H$ distance is probably unfavorable for chelation to the metal. In $B_3H_7 \cdot P(CH_3)_3$ the vicinal $H \cdots H$ distance would be comparable to that in $B_2H_4 \cdot 2P(CH_3)_3$. However, because of the lack of electron density, the hydrogen atoms would not be sufficiently hydridic for the complex to form. The behaviors of the BH_3 and B_3H_7 phosphine adducts also contrast with the known abilities of the BH_4^- and $B_3H_8^-$ anions to form bidentate chelate complexes. The anionic charge is thought to facilitate the coordination to metals.

Similar ligand behavior is expected of the other electron sufficient borane adducts. At this time, characterization of the complexes of this category is not complete. However, an aspect of this coordination chemistry was demonstrated in the following observation. When zinc chloride was added to a 1:1 molar mixture of $B_2H_4 \cdot 2P(CH_3)_3$ and $B_3H_5 \cdot 3P(CH_3)_3$ in cold dichloromethane, zinc chloride combined preferentially with the triborane adduct. The zinc-triborane complex was insoluble in diethyl ether, and therefore could be separated at low temperatures from the unchanged

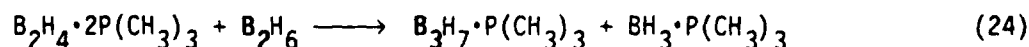
$B_2H_4 \cdot 2P(CH_3)_3$ as a solid which was unstable at room temperature. The flexible "bite" distance and the enhanced hydridic character of hydrogen atoms in $B_3H_5 \cdot 3P(CH_3)_3$ are thought to contribute to the added stability of the complex at low temperatures.

4.3. Borane Expansion Reaction

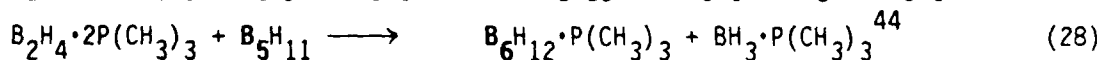
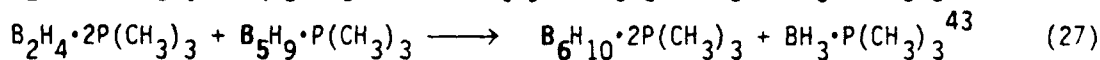
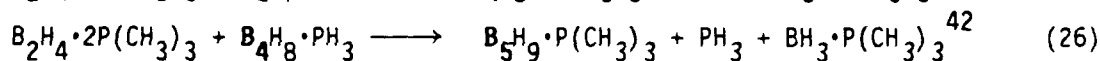
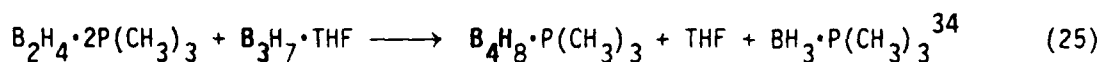
The $B_2H_7^-$ salt of the triboron complex cation decomposes at room temperature according to the following equation³¹:



Therefore, the equation for the overall reaction of $B_2H_4 \cdot 2P(CH_3)_3$ with diborane(6) at room temperature is



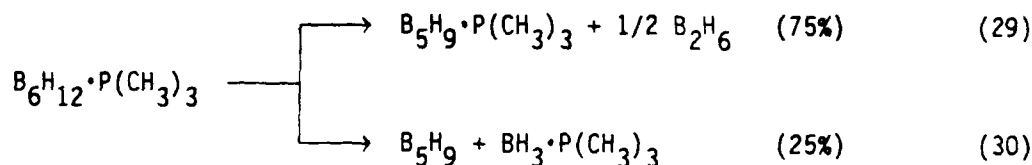
In this reaction, a two-boron species B_2H_6 is converted into a three-boron species $B_3H_7 \cdot P(CH_3)_3$. The borane framework is expanded by one boron atom. The generality of this borane expansion is demonstrated by the following reactions:



In effect, $B_2H_4 \cdot 2P(CH_3)_3$ breaks up into $BH \cdot P(CH_3)_3$ and $BH_3 \cdot P(CH_3)_3$, and the $BH \cdot P(CH_3)_3$ portion adds to the borane substrate to form the trimethylphosphine adduct of the expanded borane. Although the weak base adducts of B_3H_7 or B_4H_8 undergo the expansion reaction as indicated above,

trimethylamine and trimethylphosphine adducts of the same boranes do not react with $B_2H_4 \cdot 2P(CH_3)_3$. Presumably, the borane substrates need to have a certain degree of acidity, or electrophilicity, in order to undergo the reaction with $B_2H_4 \cdot 2P(CH_3)_3$. Generally, as the size of the borane-cage structure becomes larger, the acidity of the borane increases.⁵ Thus, $B_5H_9 \cdot P(CH_3)_3$ is acidic enough to undergo the expansion reaction with $B_2H_4 \cdot 2P(CH_3)_3$, whereas the trimethylphosphine adducts of tri- and tetraboranes are not acidic enough to react.

The reaction of pentaborane(11) with $B_2H_4 \cdot 2P(CH_3)_3$ proceeded rapidly at $-80^\circ C$ to give the expanded adduct $B_6H_{12} \cdot P(CH_3)_3$.⁴⁴ This compound was identified originally by J.R. Long in Shore's laboratory as the product of trimethylphosphine addition to B_6H_{12} .⁴⁵ At higher temperatures this adduct undergoes two simultaneous decomposition reactions.



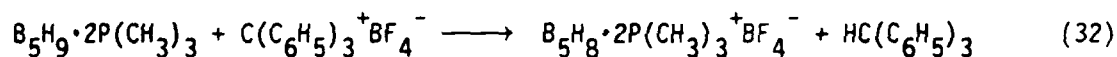
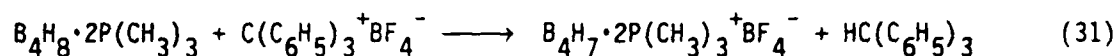
Thus, the overall reaction of pentaborane(11) with $B_2H_4 \cdot 2P(CH_3)_3$ serves as an alternative, practical method for the preparation of $B_5H_9 \cdot P(CH_3)_3$. This mono-adduct of B_5H_9 cannot be prepared by the direct reaction of pentaborane(9) with trimethylphosphine.

5. POLYBORON COMPLEX CATIONS

Formation of the triboron complex cation $B_3H_6 \cdot 2P(CH_3)_3^+$ was described in Section 4.1. The cation represented a member of a new generation of

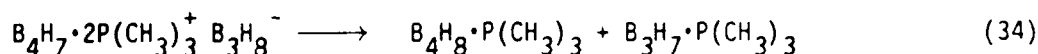
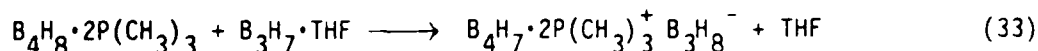
borane compounds, and the isolation and characterization of this new cation completed the isoelectronic and isostructural trio, $B_3H_6 \cdot 2P(CH_3)_3^+$, $B_3H_7 \cdot P(CH_3)_3$ and $B_3H_8^-$. It was of interest to establish the other members of this new family of cationic species with the general formula $B_nH_{n+3} \cdot 2P(CH_3)_3^+$, and to investigate the structural correlations with the isoelectronic species, $B_nH_{n+4} \cdot P(CH_3)_3$ and $B_nH_{n+5}^-$.

For the same reason discussed earlier, the hydrogen atoms in the hypho class trimethylphosphine adducts of boranes were expected to have an enhanced hydridic character, and therefore the facile removal of a hydrogen atom as H^- from these adducts was anticipated. Indeed, the trityl cation could successfully be used to abstract a hydride ion from $B_4H_8 \cdot 2P(CH_3)_3$ and $B_5H_9 \cdot 2P(CH_3)_3$, and thus the desired cations were obtained.^{46,47}



These reactions proceeded at $-80^\circ C$ in dichloromethane. The BF_4^- salt of the tetraboron complex cation $B_4H_7 \cdot 2P(CH_3)_3^+$ was a stable solid at room temperature in the absence of air. The salt of the pentaboron complex cation $B_5H_8 \cdot 2P(CH_3)_3^+$, however, was stable only below $-30^\circ C$ and decomposed readily at room temperature. These cations were very sensitive to moisture and formed the $B_3H_6 \cdot 2P(CH_3)_3^+$ and $B_4H_7 \cdot 2P(CH_3)_3^+$ cations, respectively, when exposed to a slight amount of moisture.

Hydride removal could also be effected by $B_3H_7 \cdot THF$ on $B_4H_8 \cdot 2P(CH_3)_3$ in dichloromethane at $-10^\circ C$ as evidenced by the formation of $B_4H_7 \cdot 2P(CH_3)_3^+B_3H_8^-$. However, above $20^\circ C$ an exchange reaction proceeded slowly between the cation and the anion.⁴⁶

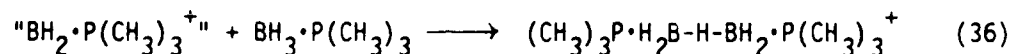
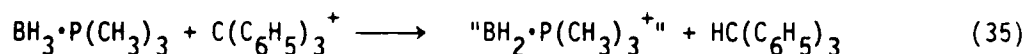


The pentaborane adduct $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$ would not yield H^- to $\text{B}_3\text{H}_7 \cdot \text{THF}$ in the temperature range where the pentaboron complex cation was stable. At higher temperatures a complex mixture of borane compounds was produced.

The NMR spectra of the tetraboron cation indicate⁴⁶ that its structure is of C_1 symmetry, and are consistent with the structure shown in Figure 5, which can be derived from the structures of isoelectronic sister compounds $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$ and B_4H_9^- . Thus, the isoelectronic and isostructural feature for the arachno tetraboron trio is apparent. Similarly, the structure of the $\text{B}_5\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3^+$ cation is of C_1 symmetry, and is isostructural with $\text{B}_5\text{H}_9 \cdot \text{P}(\text{CH}_3)_3$ ^{44,45}, and probably with the $\text{B}_5\text{H}_{10}^-$ anion⁴⁸ also. See Figure 5. It is noted that, within each of the trios, the anion is most fluxional, and the fluxionality decreases as the negative charge is reduced by replacing H^- with trimethylphosphine. Rapid and extensive migration of hydrogen atoms is observed only in the $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_3^+$ cation at room temperature; the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+$ and $\text{B}_5\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3^+$ cations are non-fluxional.

The reaction of $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ with trityl tetrafluoroborate in dichloromethane was of interest because it gave a product which was tentatively assigned as the BF_4^- salt of $\text{B}_2\text{H}_5 \cdot 2\text{P}(\text{CH}_3)_3^+$. The compound decomposed above -40°C , and $\text{BF}_3 \cdot \text{P}(\text{CH}_3)_3$ and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ were produced. Although the full characterization of the cationic species is not complete yet, the ^1H NMR spectrum of freshly prepared solutions containing the product clearly showed the presence of the bridge hydrogen atom (at -1.88 ppm) as well as the terminal hydrogen atoms (at 3.27 ppm). In 1970, Benjamin and

coworkers⁴⁹ treated Lewis base adducts of borane(3), $\text{BH}_3 \cdot \text{L}$, with trityl cation in the presence of other Lewis bases (L') to prepare monoboron complex cations with the formula $\text{BH}_2 \cdot \text{LL}'^+$. In our reaction, excess $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ is thought to be acting as the second Lewis base, the terminal hydrogen being the base site. The terminal hydrogen coordinate to the cationic center forming a BHB three-center bond:



The above diboron complex cation is isoelectronic and isostructural with the B_2H_7^- anion which has been established⁵⁰. See Figure 5.

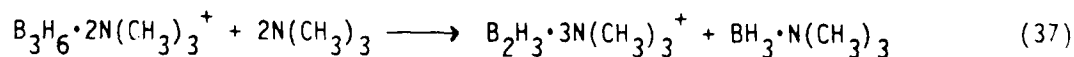
6. SUMMARY AND PERSPECTIVES

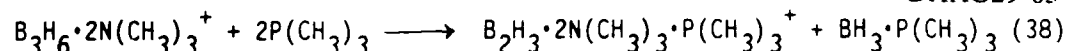
Contrary to the common impression of the early days, reactions of certain boranes with excess trimethylphosphine proceeded in simple and definable manners. By virtue of its strong donor character, trimethylphosphine was able to completely remove the "electron deficiency" from the boranes that were studied. The properties of some stable trimethylphosphine adducts were exploited to establish new reactions and compounds.

The working model used in pursuing the above study was the following: (1) Trimethylphosphine, upon combining with borane fragments, would form B-P bonds strong enough to prevent the dissociation of the adducts. This dissociation often induced secondary reactions that were detrimental to the positive identification of reactions and products. (2) In an adduct,

trimethylphosphine would donate sufficient electron density to the borane moiety to enhance the hydridic character of borane hydrogen atoms and to make the adduct susceptible to electrophilic species. The new cleavage reactions with trimethylphosphine and the new trimethylphosphine adducts of boranes stemmed from the first part of the model. The second part of the model led to the coordination of a neutral borane adduct through the formation of B-H-M bonds, the facile abstraction of H^- from the adducts to form the polyboron complex cations, and the borane expansion reactions involving $B_2H_4 \cdot 2P(CH_3)_3$. Thus, the use of trimethylphosphine was a success in unveiling several facets of the reaction chemistry of smaller boranes.

Obviously, many details of the results need to be investigated, and each of the newly discovered facets has to be projected further along the line of its development to enrich that area of chemistry and to delineate the extent of the validity of the working model. While these aspects warrant further investigation and are being explored, studies of reactions which involve other Lewis bases have become more interesting and promising than they were before. Recently in this laboratory, R.E.DePoy isolated the bis(trimethylamine) adduct of diborane(4), $B_2H_4 \cdot 2N(CH_3)_3$, as a stable solid.⁵¹ This compound reacted with electrophilic reagents in much the same way as $B_2H_4 \cdot 2P(CH_3)_3$ did: It formed a complex with zinc chloride, and reacted with diborane(6) and tetraborane(10) to give $B_3H_6 \cdot 2N(CH_3)_3^+ B_2H_7^-$ and $B_3H_6 \cdot 2N(CH_3)_3^+ B_3H_8^-$, respectively. This cation in the $B_3H_8^-$ salt, however, reacted with strong bases differently than the $B_3H_6 \cdot 2P(CH_3)_3^+$ cation did.⁵¹ (Compare the following reactions with equation 17).





The diboron complex cations produced in these reactions are members of yet another new family of cations $\text{B}_n\text{H}_{n+1} \cdot 3\text{L}^+$ (L = Lewis base). These new findings represent examples of areas of future development. The nature of the base involved in a borane adduct subtly influences the reactivity of the adduct. The knowledge gained from the trimethylphosphine systems will provide valuable insights into new findings, and will serve as a useful guide for furthering the investigations.

Finally, the work described in this chapter represents an extension of Professor Burg's earlier studies on the reactions of boranes with Lewis bases. Experiments carefully executed by skilled hands and precise descriptions of the results have always been a characteristic of his work. Because of this, his work has been a source of valuable knowledge to the succeeding generation. Thus, we who participated in this study have benefited greatly from his work, and are very fortunate to have had such a dedicated person as a pioneer in this area of chemistry. It is indeed my pleasure to present this chapter as a token of appreciation to Professor Burg for his accomplishments in the field of boron hydride chemistry, and I am grateful to the members of the editorial committee of this book for giving me this opportunity.

ACKNOWLEDGMENT

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Robert W. Parry for his stimulating discussions and moral support that made the performance of this research possible.

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Captions to the Figures

- Figure 1. ^{11}B NMR spectra of $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$, 32.1 MHz.
- Figure 2. ^{11}B NMR spectra of $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3 \cdot \text{N}(\text{CH}_3)_3$, 32.1 MHz.
The arrow indicates the presence of $\text{BH}_3 \cdot \text{N}(\text{CH}_3)_3$ impurity.
- Figure 3. Structure of $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_3^+ \text{B}_3\text{H}_8^-$. Orthorhombic, A2122.
- Figure 4. Molecular structure of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3 \cdot \text{ZnCl}_2$.
- Figure 5. Isoelectronic and isostructural feature of arachno trios.

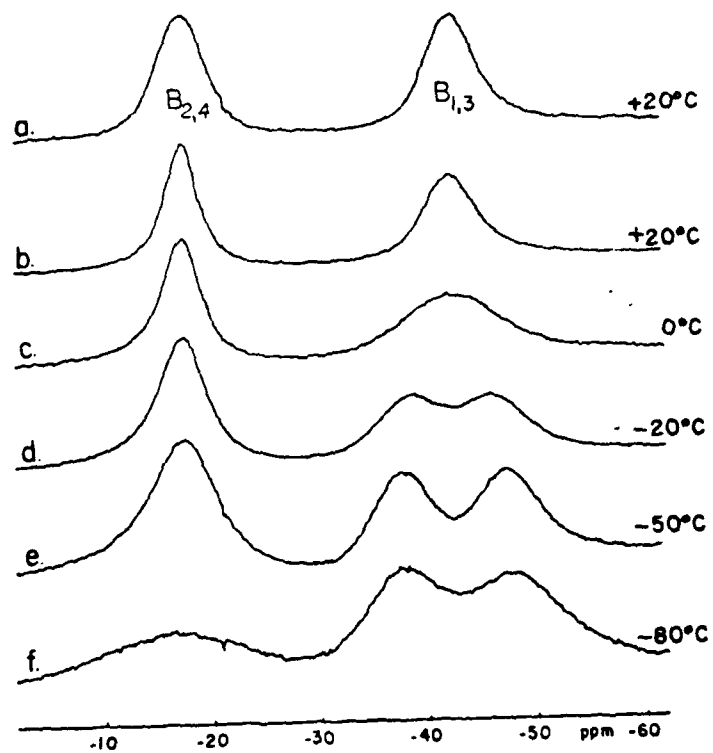


Figure 1.

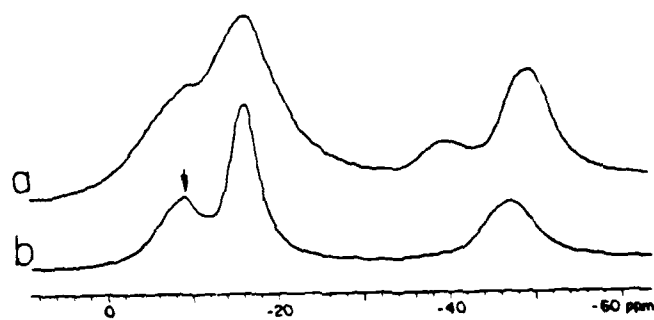


Figure 2.

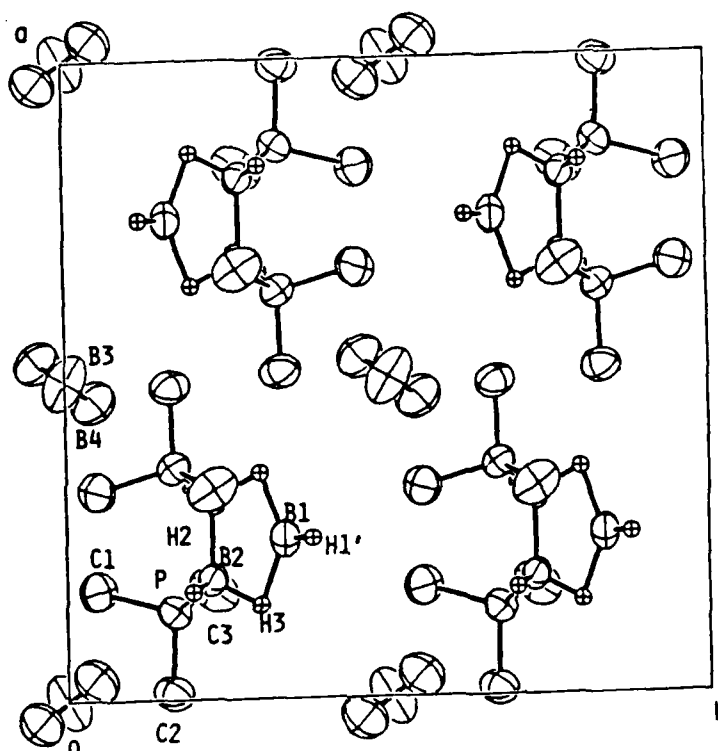


Figure 3.

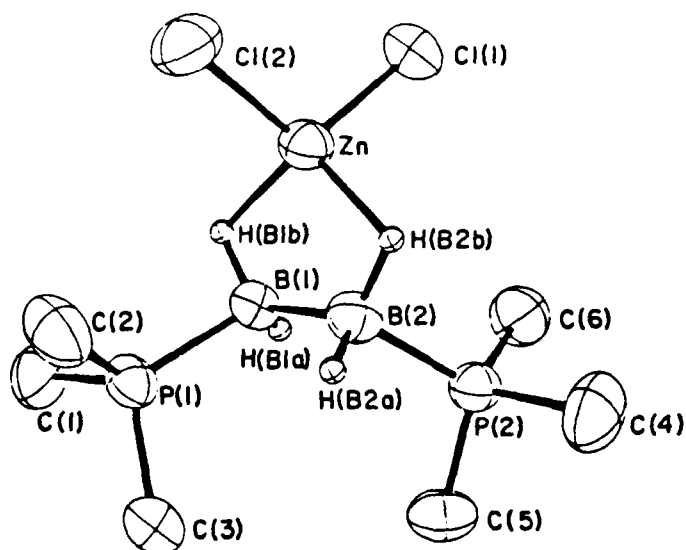


Figure 4.

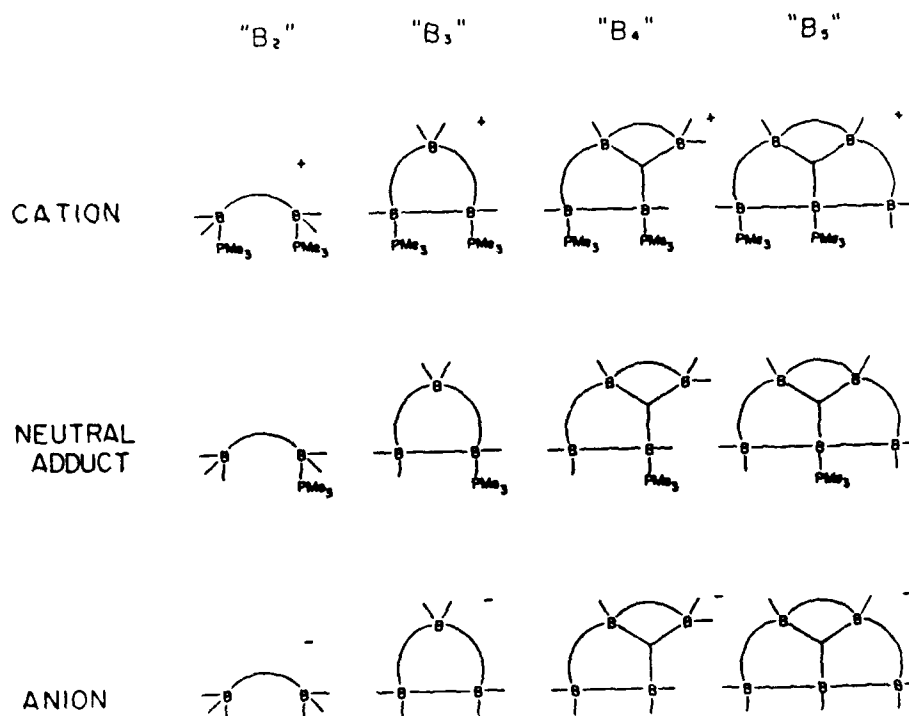


Figure 5.

POLYBORON COMPLEX CATIONS -
A RECENT DEVELOPMENT IN LOWER BORANE CHEMISTRY

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ABSTRACT. In the past several years, a new class of boron hydride compounds, polyboron complex cations, was developed in the department of chemistry at the University of Utah. These cations include $B_nH_{n+3} \cdot 2L^+$, $B_nH_{n+3} \cdot L^+$, $B_nH_{n+1} \cdot 3L^+$ and $B_nH_{n+1} \cdot 4L^+$. Formation, structures and reactivities of the cations are briefly reviewed.

1. INTRODUCTION

Several years ago, we decided to look into the reaction chemistry of the trimethylphosphine adduct of diborane(4), $B_2H_4 \cdot 2P(CH_3)_3$. Unlike most borane compounds, the adduct is an electron precise compound, and additionally, two trimethylphosphine molecules are attached to it. Because of its lack of "electron deficiency" and the coordination of the strongly electron donating trimethylphosphine ligand, the B_2H_4 moiety was expected to show enhanced reactivities toward electrophilic reagents. The study was rewarding in that it yielded the following three major findings: [1] A triboron complex cation, $B_3H_6 \cdot 2P(CH_3)_3^+$, was formed by treating the diborane(4) adduct with diborane(5) or tetraborane(10);¹⁾ [2] metal complexes of the diborane(4) adduct were formed by the coordination of the diborane(4) adduct to metal centers via two $B-H \rightarrow M$ bridge bonds;²⁾ [3] borane cluster expansion was observed when certain borane substrates were treated with the diborane(4) adduct.³⁾ Each of these findings was significant enough to be developed into a new area of boron hydride chemistry.

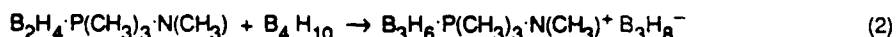
The $B_3H_6 \cdot 2P(CH_3)_3^+$ cation was the first example of a polyboron complex cation. Although mono-

boron complex ("boronium") cations with the general formula $H_2B \cdot L \cdot L^+$ (L and L^+ =Lewis bases) have been studied extensively,⁴⁾ other cationic lower borane species were virtually nonexistent. The sole representative case was the formation of $B_6H_{11}^+$, reported by Shore.⁵⁾ While reaction chemistry of the bis(trimethylphosphine)triboron(1+) cation was investigated and syntheses of other bis(trimethylphosphine)polyboron(1+) cations were being explored, new diborane(4) adducts, $B_2H_4 \cdot 2N(CH_3)_3$ and $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$,⁶⁾ were synthesized. These adducts were found to produce two new triboron complex cations, $B_3H_6 \cdot 2N(CH_3)_3^+$ ⁶⁾ and $B_3H_6 \cdot N(CH_3)_3 \cdot P(CH_3)_3^+$ ⁷⁾ when treated with B_2H_6 or B_4H_{10} . The formation of these cations which contain trimethylamine provided a valuable opportunity for investigating the effects of the coordinated ligand on the chemical behavior of triboron cations. In this paper we wish to present an "interim" review of the development of polyboron complex cation chemistry that followed the discovery of the $B_3H_6 \cdot 2P(CH_3)_3^+$ cation.

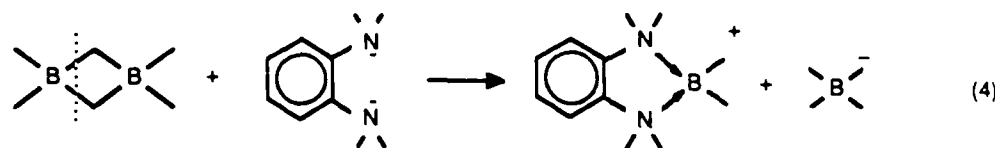
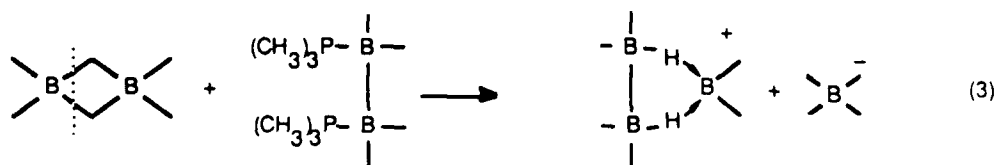
2. FORMATION OF POLYBORON COMPLEX CATIONS

2.1 Addition of BX_2^+ to B_2H_4 Adducts — Formation of Triboron Complex Cations

The reaction of $B_2H_4 \cdot 2P(CH_3)_3$, $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ or $B_2H_4 \cdot 2N(CH_3)_3$ with diborane(6) or tetraborane(10) proceeds in the manners indicated in Equations 1 and 2.^{6,7)} The $B_2H_7^-$ salts are unstable at room temperature and decompose to give the triborane(7) adducts. (See Section 4.) The $B_3H_8^-$ salts are reasonably stable at room temperature.



These reactions may be regarded as an "unsymmetrical cleavage" of diborane(6) or tetraborane(10) by a special bidentate ligand, $B_2H_4 \cdot 2P(CH_3)_3$. Indeed, the feature of chelate coordination of $B_2H_4 \cdot 2P(CH_3)_3$ to the BH_2^+ unit through two $B-H \rightarrow B$ bridge bonds is seen in the structure of the cation (Figure 1). The situation is similar to the coordination of diamines to BH_2^+ .⁸⁾ See Equations 3 and 4.

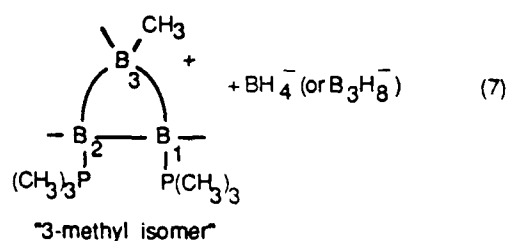
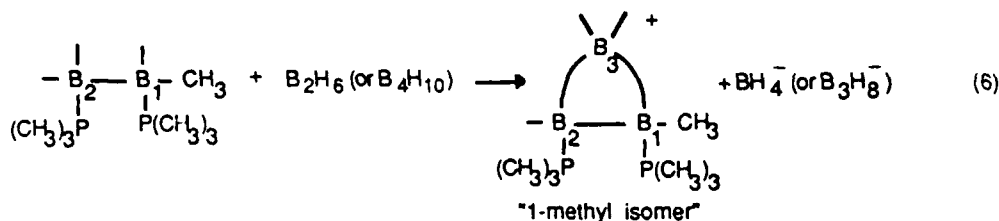


Likewise, $B_2H_4 \cdot 2P(CH_3)_3$ reacts with boron trifluoride to give an unstable fluoro derivative of the triboron complex cation.^{1,9)}



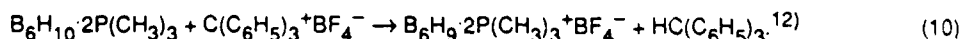
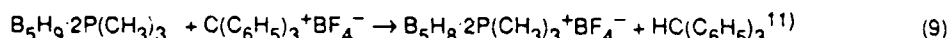
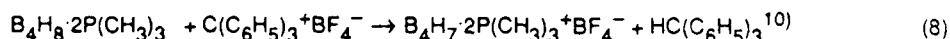
In this cation also, the BF_2^+ unit is thought to be coordinated by $B_2H_4 \cdot 2P(CH_3)_3$ through two B—H→B bridge bonds.

The methyl derivative of the diborane(4) adduct, $CH_3B_2H_3 \cdot 2P(CH_3)_3$, reacts with B_4H_{10} to give the $B_3H_8^-$ salt of methyl derivatives of the triboron complex cation.^{1,9)} The 1,2-bis(trimethylphosphine)-1-methylpentahydrotriboron(1+) cation which is formed initially at low temperature undergoes rearrangement above $-40^\circ C$ to give 1,2-bis(trimethylphosphine)-3-methylpentahydrotriboron(1+), as illustrated in Equations 6 and 7.



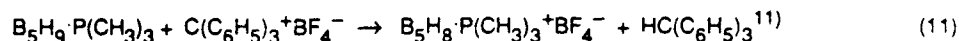
2.2 Hydride Abstraction from Neutral Trimethylphosphine Adducts of Boranes

Treatments of bis(trimethylphosphine) adducts of boranes with triphenylcarbenium (trityl) tetrafluoroborate result in the formation of corresponding polyboron complex cations. The following reactions have been established:



The salts of these polyboron complex cations decompose slowly at room temperature, but are stable enough for structural characterization by NMR spectroscopy. The structures proposed for these cations are shown in Figure 2 and will be discussed in Section 3. Likewise, the uni(trimethylphosphine) adduct of

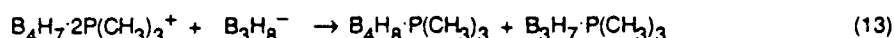
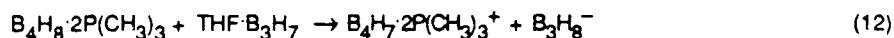
pentaborane(9) reacts with trityl cation, and the corresponding cation containing one phosphine ligand is produced (Equation 11). This reaction proceeds less readily than the reaction of $B_5H_9 \cdot 2P(CH_3)_3$



(Equation 9), reflecting the less hydridic character of the borane hydrogens in the uni(phosphine) adduct relative to that of the bis(phosphine) adduct. Although the reactions of the trimethylphosphine adducts occur considerably below 0 °C, B_5H_9 will not react with the trityl cation even at room temperature.¹¹⁾

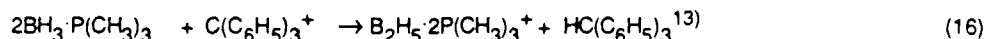
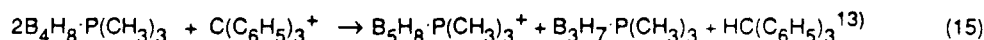
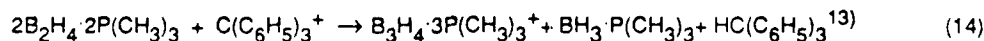
Trityl hexafluorophosphate, $C(C_6H_5)_3^+ PF_6^-$, also abstracts hydride ions from the phosphine adducts of boranes which are listed above. However, the PF_6^- ion reacts with these borane substrates and, in particular, with the cationic products to produce $BF_3 \cdot P(CH_3)_3$ and BF_4^- . Therefore, the use of $C(C_6H_5)_3^+ PF_6^-$ is not recommended for the preparation of the polyboron complex cations.^{11,12)}

Tetrahydrofuran-triborane(7) can also abstract a hydride ion from $B_4H_8 \cdot 2P(CH_3)_3$ to give the $B_4H_7 \cdot 2P(CH_3)_3^+$ cation at -10 °C. At higher temperatures the cation is converted into $B_4H_8 \cdot P(CH_3)_3$ by a ligand exchange reaction as shown in Equation 13.¹¹⁾

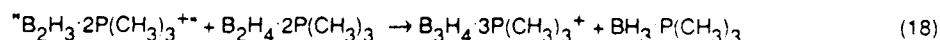
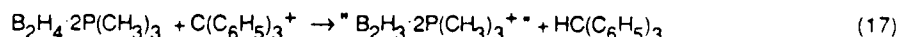


2.3 Hydride Abstraction Followed by Secondary Reactions

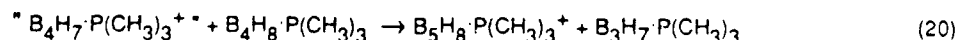
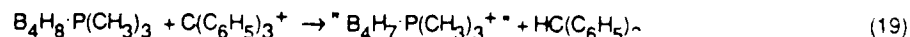
Certain polyboron complex cations are formed as the result of secondary reactions that follow after the initial hydride removal from the neutral borane adducts. Examples are given in the following equations:



In the reaction shown in Equation 14, the diborane(4) adduct is thought to be converted into a reactive intermediate cationic species " $B_2H_3 \cdot 2P(CH_3)_3^+$ " (Equation 17), which then undergoes a cluster expansion reaction with $B_2H_4 \cdot 2P(CH_3)_3$ (Equation 18).



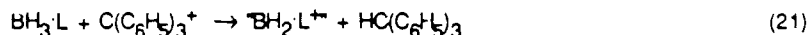
Similarly, the formation of $B_5H_8 \cdot P(CH_3)_3^+$ in Equation 15 is thought to have proceeded through the formation of a reactive intermediate " $B_4H_7 \cdot P(CH_3)_3^+$ " (Equation 19).



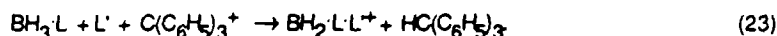
It is worth noting that, in Equation 20, $B_4H_8 \cdot P(CH_3)_3$ is acting as a borane cluster expansion reagent by converting itself into $B_3H_7 \cdot P(CH_3)_3$ and thus providing a "BH" unit to the substrate, $B_4H_8 \cdot P(CH_3)_3$, for

framework expansion. This is similar to the behavior of $B_2H_4 \cdot 2P(CH_3)_3$ which adds a " $BH \cdot P(CH_3)_3$ " unit to borane substrates by converting itself into $BH_3 \cdot P(CH_3)_3$. [See, for example, Equation 18.] This mode of cluster expansion, which is accompanied by the elimination of a stable Lewis base adduct, deserves further investigation, as it appears to be one of the fundamental reactions of boron hydride chemistry.

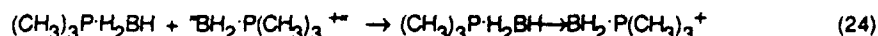
The reaction in Equation 16 is also thought to involve a reactive intermediate " $BH_2 \cdot P(CH_3)_3$ ", and is thus an extension of the reactions reported by Benjamin, Calvalho, Stafiej and Takacs for the preparation of boronium cations, $BH_2 \cdot L^+$.¹⁴⁾



Thus, the overall reaction is



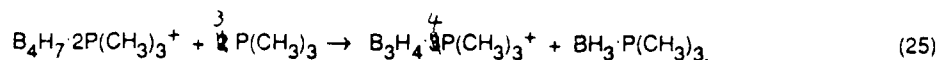
In the reaction of $BH_3 \cdot P(CH_3)_3$ with the trityl cation in the presence of excess $BH_3 \cdot P(CH_3)_3$, the second molecule of $BH_3 \cdot P(CH_3)_3$ plays the role of L' by coordinating to " $BH_2 \cdot P(CH_3)_3$ " through the formation of a $B-H \rightarrow B$ bridge bond.



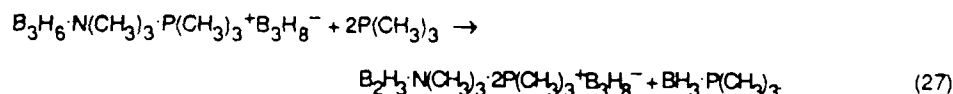
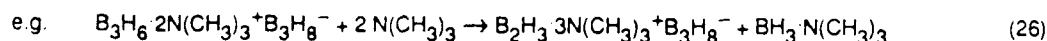
The characterization of this very unstable diboron complex cation, $B_2H_5 \cdot 2P(CH_3)_3^+$, has yet to be completed. However, ^{11}B , 1H and ^{31}P NMR spectra of the reaction mixtures suggest that the product of reaction is the diboron cation, $(CH_3)_3P \cdot H_2B-H-BH_2 \cdot P(CH_3)_3^+$, with a structure analogous to that of the isoelectronic species, $B_2H_7^-$.

2.4 Cleavage of Polyboron Complex Cations with Lewis Bases

Like neutral and anionic boron hydride compounds, the polyboron complex cations, if electron deficient, undergo cleavage or addition reactions with Lewis bases. Thus, the tetraboron cation $B_4H_7 \cdot 2P(CH_3)_3^+$ is cleaved (a "symmetrical" cleavage) by trimethylphosphine according to the following equation:¹³⁾



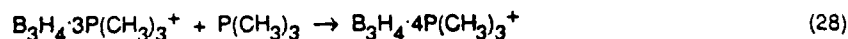
Similarly, when the $B_3H_8^-$ salts of the amine-containing cations, $B_3H_6 \cdot 2N(CH_3)_3^+$ and $B_3H_6 \cdot N(CH_3)_3 \cdot P(CH_3)_3^+$, are treated with $N(CH_3)_3$ or $P(CH_3)_3$, the cations are cleaved and the diboron complex cations are formed with the general formula $B_2H_3 \cdot (3-x) \cdot N(CH_3)_3 \cdot xP(CH_3)_3^+$.^{5,7)}



In contrast, the treatment of $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$ with $P(CH_3)_3$ or $N(CH_3)_3$, does not give the expected diboron cation $B_2H_3 \cdot 3P(CH_3)_3^+$ or $B_2H_3 \cdot 2P(CH_3)_3 \cdot N(CH_3)_3^+$.¹⁵⁾ See Section 4.

2.5 Lewis Base Addition to Polyboron Complex Cations

Although this is another general type of reaction, so far only one example can be cited.



The product cation is an electron precise, hypoh class species and is stable toward trimethylphosphine.¹³⁾

3. STRUCTURES OF POLYBORON COMPLEX CATIONS

3.1 $B_nH_{n+3} \cdot 2P(CH_3)_3^+$

An x-ray diffraction analysis has been performed on a single crystal of $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$ at $-90^\circ C$.¹⁶⁾ The structure is shown in Figure 1. The geometries of the two isoelectronic triboron species,

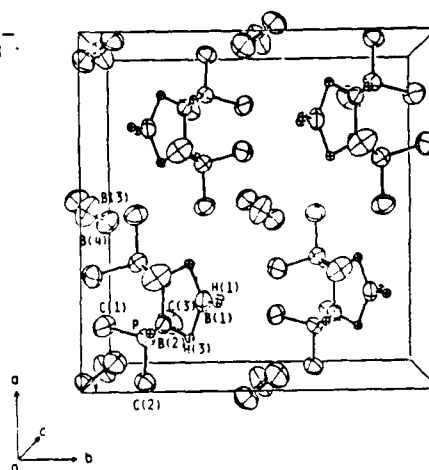
Unit cell packing of $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$.

Orthorhombic:

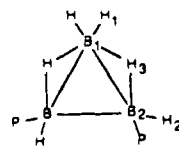
$$a = 14.063(4) \text{ \AA}$$

$$b = 14.191(3) \text{ \AA}$$

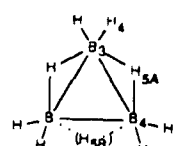
$$c = 8.784(2) \text{ \AA}$$



Bond lengths (Å) for $B_3H_6 \cdot 2P(CH_3)_3^+$ and $B_3H_8^-$.



| | |
|------------|----------|
| B(1)-B(2) | 1.805(6) |
| B(2)-B(2') | 1.805(6) |
| B(1)-H(1) | 1.10(4) |
| B(1)-H(3) | 1.40(3) |
| B(2)-H(3) | 1.13(3) |
| B(2)-H(2) | 1.13(3) |
| B(2)-P | 1.906(4) |



| | |
|------------|----------|
| B(3)-B(4) | 1.769(7) |
| B(4)-B(4') | 1.773(9) |
| B(3)-H(4) | 1.04(4) |
| B(3)-H(5A) | 1.35(9) |
| B(4)-H(5A) | 1.35(11) |
| B(4)-H(6) | 1.18(5) |
| B(4)-H(7) | 1.00(4) |
| B(4)-H(5B) | 1.40(8) |

Figure 1. Structure of $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$.

$B_3H_6 \cdot 2P(CH_3)_3^+$ and $B_3H_8^-$ are similar to each other. Slightly longer B-B distances for the cation are noted. The cation is fluxional with respect to the migration of all borane hydrogen atoms around the three-boron framework: The room temperature 1H NMR spectrum shows only one signal for the borane hydrogen atoms. At $-80^\circ C$, however, the signal is split into three signals of equal intensity, which is expected for the static structure shown in the figure.¹⁾ The cation is less fluxional than $B_3H_7 \cdot P(CH_3)_3$ which is less fluxional than the $B_3H_8^-$ anion; the 1H NMR signals for the static structure of $B_3H_7 \cdot P(CH_3)_3$ can only be observed when the sample is cooled to $-95^\circ C$,¹⁷⁾ and at this temperature the 1H spectrum of the $B_3H_8^-$ anion indicates that the hydrogen atoms are rapidly migrating.

The structures proposed for the $B_nH_{n+3} \cdot 2P(CH_3)_3^+$ homologs are summarized in Figure 2. Shown also in the figure are the reported structures of related isoelectronic, neutral and anionic species.^{12,18-20)} Clearly, each of the cations is isostructural with its isoelectronic counterparts. In the NMR spectra of the tetra-, penta- and hexaboron cations, no indication of rapid fluxional behavior is observed up to room temperature, whereas every one of the corresponding isoelectronic species is known to exhibit fluxional behavior.

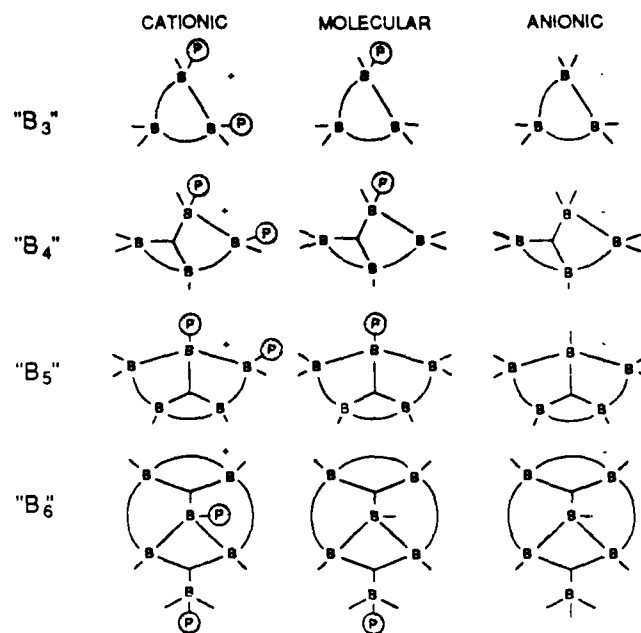


Figure 2. Structures of the $B_nH_{n+3} \cdot 2P(CH_3)_3^+$ cations and related isoelectronic, neutral and anionic species. The shaded circles represent $P(CH_3)_3$.

3.2 $B_nH_{n+3} \cdot P(CH_3)_3^+$

The ^{11}B NMR spectra of $B_5H_8 \cdot P(CH_3)_3^+$ (Figure 3), and the $^1H\{^{11}B\}$ spectrum of the cation, which contains two borane hydrogen signals (terminal and bridging) in a 1:1 intensity ratio, immediately suggest that the structure of the cation is as illustrated in Figure 3.¹¹⁾ Thus, it is isostructural with pentaborane(9) which is isoelectronic with the cation. The B-P coupling constants of the apex boron atom in the square pyramid structures are unusually large. The values of 220 and 212 Hz are observed for $B_5H_8 \cdot P(CH_3)_3^+$ ¹¹⁾ and $B_6H_9 \cdot 2P(CH_3)_3^+$,¹²⁾ respectively.

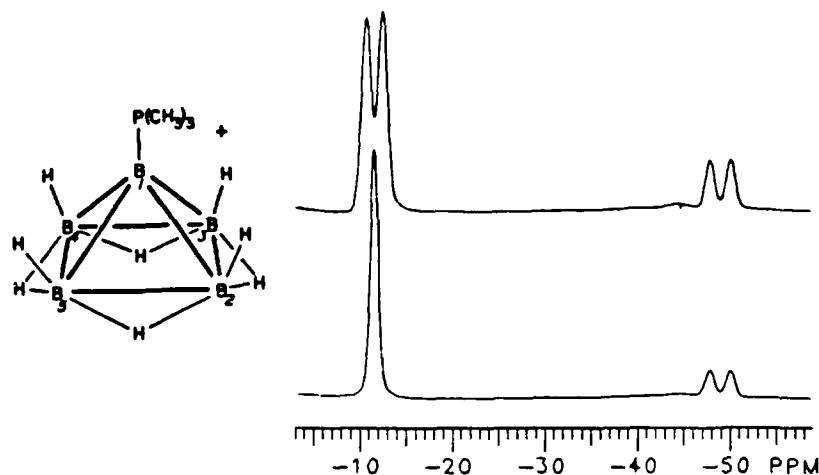


Figure 3. ^{11}B NMR spectra and proposed structure of $B_5H_8 \cdot P(CH_3)_3^+$.
Upper spectrum, 1H -spin coupled; lower spectrum, 1H -spin decoupled.

3.3 $B_nH_{n+1} \cdot 3L^+$

Four of the six possible $B_2H_3(3-x)N(CH_3)_3 \cdot xP(CH_3)_3^+$ cations where $x=0,1$ and 2 have been prepared and the structures studied by NMR spectroscopy.^{6,7)} See Figure 4. These cations are electron precise, and are isoelectronic with $B_2H_4 \cdot 2P(CH_3)_3$ and $B_2H_4 \cdot 2N(CH_3)_3$.

The $B_3H_4 \cdot 3P(CH_3)_3^+$ cation has the structure shown in Figure 5, which is consistent with its low temperature ($-100^\circ C$) ^{11}B , 1H and ^{31}P NMR spectra.¹³⁾ At room temperature, however, the cation is fluxional with respect to the rapid migration of all four borane hydrogen atoms around the borane framework: The signals of borane hydrogen atoms are coalesced to a single signal, as are the ^{11}B and ^{31}P signals. To illustrate the fluxional behavior of this cation, a process involving an intermediate, which contains a coordinated double bond, is proposed. See Scheme 1. Such a coordinated double bond

representation has been used to describe the valence bond structure of $B_4C_2H_8$.²¹⁾

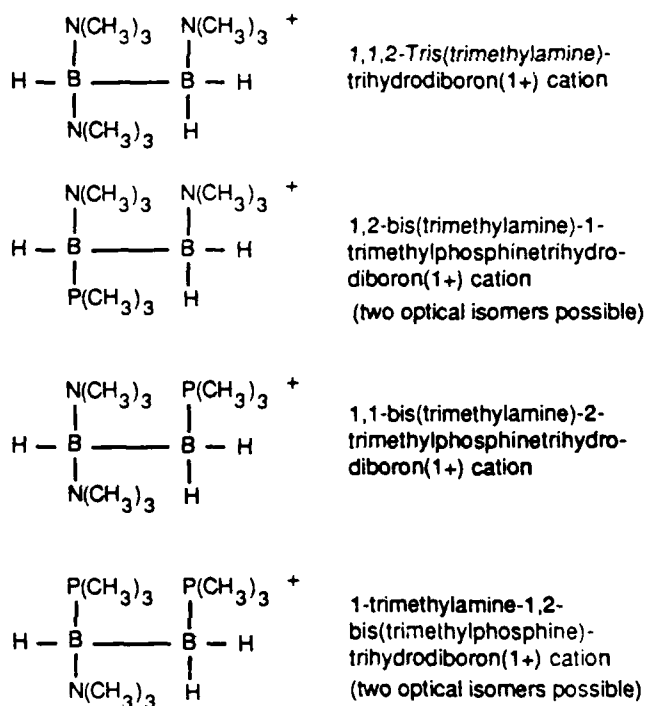


Figure 4. Diboron complex cations, $B_2H_3 \cdot (3-x)N(CH_3)_3 \cdot xP(CH_3)_3^+$, where $x=0, 1$ and 2 .

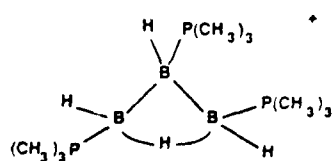


Figure 5. Structure proposed
for $B_3H_4 \cdot 3P(CH_3)_3^+$

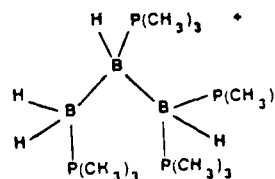
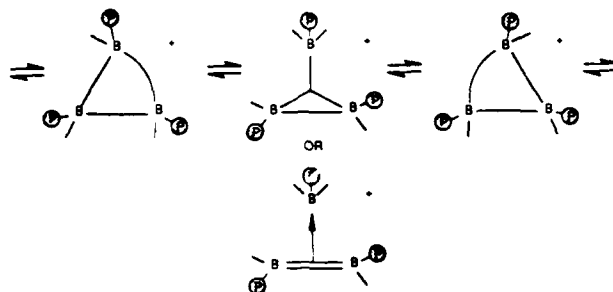


Figure 6. Structure proposed
for $B_3H_4 \cdot 4P(CH_3)_3^+$

Scheme 1



3.4 $B_nH_{n+1} \cdot 4L^+$

The NMR data (^{11}B , 1H and ^{31}P) for the $B_3H_4 \cdot 4P(CH_3)_3^+$ cation¹³⁾ are consistent with the structure shown in Figure 6, which can be derived from the structure of $B_3H_4 \cdot 3P(CH_3)_3^+$ (Figure 5) by adding $P(CH_3)_3$ to one of the hydrogen bridged boron atoms, thus cleaving the bridge bond. The cation is isoelectronic with $B_3H_5 \cdot 3P(CH_3)_3$.²²⁾

3.5 Isoelectronic-Isostructural Feature

Each of the polyboron complex cations has been found to be isostructural with the isoelectronic neutral and anionic species (when those species are known). As illustrated in (i) and (ii) of Scheme 2, the structures of the tetra- and pentaboron cations are closely related to those of the respective parent compounds from which the cations are prepared. For example, the arachno $B_4H_7 \cdot 2P(CH_3)_3^+$ cation is obtained by abstracting a Lewis base, H^- , from the hypho $B_4H_8 \cdot 2P(CH_3)_3$ adduct. Conversely, the hypho adduct can be prepared by the addition of a Lewis base, $P(CH_3)_3$ to the arachno adduct, $B_4H_8 \cdot P(CH_3)_3$. The same relation also holds for the hexaboron species. However, the structural change that occurs at each step of the hexaborane transformation is seemingly drastic. It had been known, when the synthesis study of the $B_6H_9 \cdot 2P(CH_3)_3^+$ cation was initiated, that two different boron framework structures could be assumed by arachno hexaborane compounds. One was the belt-shaped structure of hexaborane(12)²³⁾ which was essentially the same as that of the hypho adduct $B_6H_{10} \cdot 2P(CH_3)_3$ ²⁴⁾ as illustrated in Figure 7(a), and the other was the basal-bridged square pyramid structure which is assumed by $B_6H_{10} \cdot P(CH_3)_3$ ¹⁹⁾ and $B_6H_{11}^-$ ²⁰⁾. Therefore, it was of interest to see how the belt-shaped structure of the hypho adduct would transform upon conversion into the arachno hexaboron cation.

The mechanism of the hexaborane structural transformation is unknown. Formation of a bond between B(2) and B(5) of the structure in Figure 7(a) followed by a succession of dsd rearrangements²⁵⁾ could result in the observed structure in Figure 7(b). As the skeletal electron-counting rule²⁶⁾ dictates, both of the two known structures of arachno hexaborane compounds are derived from the eight-vertex closo deltahedron (bisdisphenoid) by the removal of two vertices.

An obvious difference between the two sets of compounds is in the total number of ligands (including hydrogen atoms as well as bases) attached to the boron framework; eleven *versus* twelve. The less

opened structure is assumed by the eleven-ligand compound. Further studies are necessary, however, to elucidate the factors that determine the choice of structure.

Scheme 2

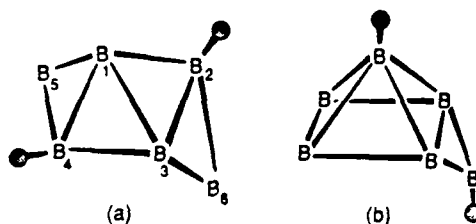
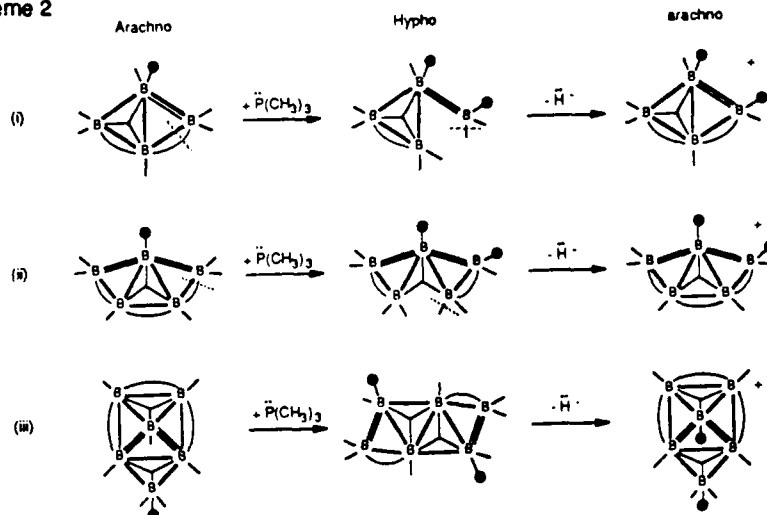


Figure 7. Boron framework structures for (a) $B_5H_{10} \cdot 2P(CH_3)_3$ and (b) $B_4H_9 \cdot 2P(CH_3)_3^+$.

4. REACTIVITIES OF POLYBORON COMPLEX CATIONS

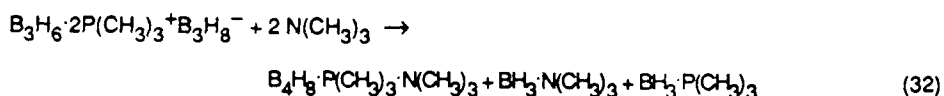
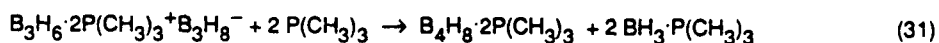
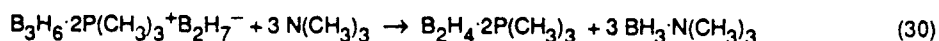
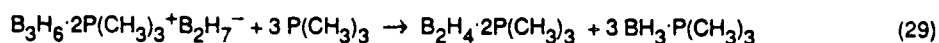
4.1 General Pattern of Reactions with Lewis Bases

The polyboron complex cations, when not electron precise, are reactive toward Lewis bases. At this stage of research, it can only be stated that trimethylphosphine either adds to the cation to form the next higher class cation (e.g. arachno \rightarrow hypho), or it cleaves the cation into $BH_3 \cdot P(CH_3)_3$ and a polyboron cation of the same class. Thus, the arachno $B_4H_7 \cdot 2P(CH_3)_3^+$ cation (as BF_4^- salt) reacts with trimethyl-

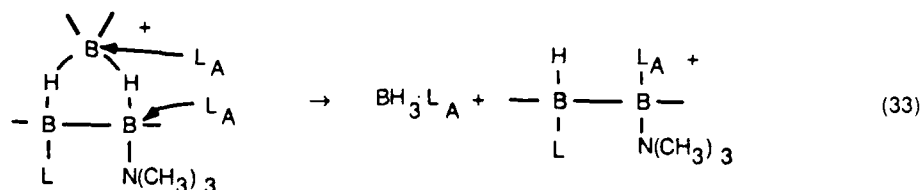
phosphine, and is cleaved into $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ and arachno $\text{B}_3\text{H}_4 \cdot 3\text{P}(\text{CH}_3)_3^+$; ¹³ the arachno $\text{B}_3\text{H}_4 \cdot 3\text{P}(\text{CH}_3)_3^+$ cation further reacts with trimethylphosphine and the hypho $\text{B}_3\text{H}_4 \cdot 4\text{P}(\text{CH}_3)_3^+$ cation is formed. ¹³ Likewise, arachno $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3^+$ reacts with $\text{P}(\text{CH}_3)_3$ to produce $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ and arachno $\text{B}_2\text{H}_3 \cdot 2\text{N}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3^+$. ⁷ The electron precise cation $\text{B}_3\text{H}_4 \cdot 4\text{P}(\text{CH}_3)_3^+$ is inert to $\text{P}(\text{CH}_3)_3$. Similarly, $\text{B}_2\text{H}_3 \cdot 3\text{N}(\text{CH}_3)_3^+$ is inert to $\text{N}(\text{CH}_3)_3$, but this cation undergoes a ligand displacement reaction with $\text{P}(\text{CH}_3)_3$ to give $\text{B}_2\text{H}_3 \cdot 2\text{N}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3^+$. ⁷ The other larger cations react with $\text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$, forming addition compounds and then further reacting with the base to produce the BH_3 adducts of the base and other borane compounds. The formation of the BH_3 adducts suggests that the original cations have undergone cleavage reactions to form new polyboron cations. Characterization of these products is not complete at this time.

4.2 Reactions of $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_3^+$, $\text{B}_3\text{H}_6 \cdot \text{N}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3^+$ and $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3^+$ with $\text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$

The reactions of $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_3^+$ with trimethylphosphine or trimethylamine are given in Equations 29-32 below. ^{1,15} Obviously, these reactions are dependent upon the hydroborate counter anions.



When B_3H_8^- is the counter anion, the product is a tetraborane(8) adduct. On the other hand, as described earlier in Equations 26 and 27, $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3^+$ and $\text{B}_3\text{H}_6 \cdot \text{N}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3^+$ react with $\text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$ to give the diboron complex cations, $\text{B}_2\text{H}_3 \cdot 2\text{L} \cdot \text{L}^+$ ($\text{L}, \text{L}^+ = \text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$) and the base adduct of BH_3 . ^{6,7} The anion is unaffected. In the products of these cleavage reactions, the attacking Lewis bases, L_A , are always attached to the BH_3 fragment and, in the diboron cation, to the boron atoms to which trimethylamine is already attached.

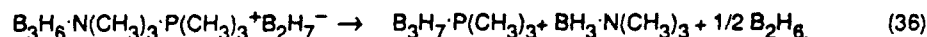
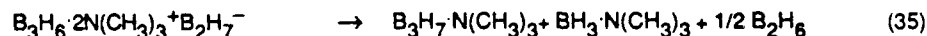
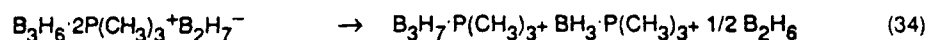


On the basis of these observations the following statement may be made. The key to the cleavage of

the triboron cation is provided by the enhanced electrophilicity of the amine attached boron atom. Trimethylphosphine does not induce such an electrophilic character in the boron atom to which it is bonded, and therefore the base attack on that boron is ineffective. A speculative mechanism for the formation of tetraborane(8) adducts from $B_3H_6 \cdot 2P(CH_3)_3^+ B_3H_8^-$ was reported elsewhere.¹⁵⁾ The mechanism includes the formation of an intermediate involving both $B_3H_6 \cdot 2P(CH_3)_3^+$ and $B_3H_8^-$, which undergoes a rapid reaction with the attacking base.

4.3 Thermal Decomposition of $B_2H_7^-$ Salts of Triboron Complex Cations

The $B_2H_7^-$ salts of the triboron cations decompose at room temperature according to the following equations:^{1,6,7)}



Thus, the overall reactions of the diborane(4) adducts with diborane(6) at room temperature is the conversion of B_2H_6 into the B_3H_7 adduct. This borane framework expansion is a general type of reaction. For example, by reaction with $B_2H_4 \cdot 2P(CH_3)_3$, $B_3H_7 \cdot THF$ and $B_4H_8 \cdot PH_3$ are converted into $B_4H_8 \cdot P(CH_3)_3$ ¹⁵⁾ and $B_5H_9 \cdot P(CH_3)_3$ ²⁷⁾ respectively. Earlier in this paper, the formation of products observed in some reactions was explained in terms of this type of reaction (Equations 18 and 20).

5. SUMMARY

Formation of a polyboron complex cation occurred when a cationic species was added to a neutral borane compound, or when an anionic species was abstracted from a neutral borane compound. Enrichment of electron density on the borane moiety of the neutral borane compound should facilitate both the addition of cationic species and the abstraction of anionic species. Thus, $B_2H_4 \cdot 2P(CH_3)_3$ combined with BH_2^+ to give the $B_3H_6 \cdot 2P(CH_3)_3^+$ cation, and the $P(CH_3)_3$ adducts of the B_4H_8 , B_5H_9 and B_6H_{10} fragments were converted into the corresponding polyboron complex cations by hydride abstraction. Subsequently, the B_2H_4 adducts which contain the $N(CH_3)_3$ ligand were also found to combine with BH_2^+ to give $B_3H_6 \cdot N(CH_3)_3 \cdot P(CH_3)_3^+$ and $B_3H_6 \cdot 2N(CH_3)_3^+$. These amine containing cations displayed reactivities which were different from those of $B_3H_6 \cdot 2P(CH_3)_3^+$. Further studies of polyboron complex cations involving characteristically different Lewis bases should enrich the reaction chemistry of boron hydrides.

Thus far, the isoelectronic-isostructural feature is prevalent among the polyboron complex cations. Also, the reaction patterns of these cationic species appear to parallel those established for the neutral

borane compounds. These apparent similarities may be developed into a working model which should prove beneficial to future exploratory work in this new area of boron hydride chemistry.

Acknowledgment. We gratefully acknowledge the support of this work by the U. S. Army Research Office through Grants DAAG 29-79-C-0129, DAAG 29-81-K-0101 and DAAG 29-85-K-0034. We thank Professor Robert W. Parry for the valuable discussions and encouragement which he constantly gave us during the performance of this research.

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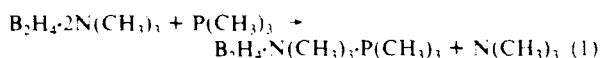
Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Formation and Reaction Chemistry of Trimethylamine-Trimethylphosphine-Diborane(4)

Rosemarie E. DePoy and Goji Kodama*

Received September 15, 1987

We reported in an earlier communication¹ to this journal that trimethylamine-trimethylphosphine-diborane(4), $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$, was formed by a ligand displacement reaction of bis(trimethylamine)-diborane(4), $B_2H_4 \cdot 2N(CH_3)_3$, with trimethylphosphine (see eq 1). The product was the first repre-

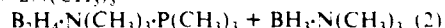


sentative of a previously unknown mixed-ligand adduct of diborane(4). Displacement of the second trimethylamine proceeded very slowly.¹

The mixed-ligand adduct, $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$, can now be prepared in pure form by the reaction of $B_3H_8 \cdot P(CH_3)_3$ with trimethylamine. Furthermore, this finding has provided a new insight into the reaction mechanism of base cleavage of triborane(7) adducts. In this paper, we describe the characterization and reaction chemistry of the mixed adduct of diborane(4).

Results

A. Cleavage of $P(CH_3)_3$ and $N(CH_3)_3$ Adducts of B_3H_8 . (a) **Reaction of $B_3H_8 \cdot P(CH_3)_3$ with $N(CH_3)_3$.** Formation of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$. The reaction of $B_3H_8 \cdot P(CH_3)_3$ with 2 molar equiv of $N(CH_3)_3$ in dichloromethane at room temperature proceeds according to eq 2. The mixed-ligand adduct of B_2H_4 can



be separated from $BH_3 \cdot N(CH_3)_3$ as a colorless solid by fractional sublimation at room temperature. The compound is stable in the absence of air. It slowly decomposes in solution at room temperature.

NMR Spectra of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$. The $^{11}B\{^1H\}$ NMR spectrum of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ in Figure 1 shows a broad signal at -2.7 ppm due to the amine-attached boron atom (B_N) and another at -36.4 ppm due to the phosphine-attached boron atom (B_P). The 1H -spin-coupled ^{11}B signals are broader but do not have any fine structure. These shift values are compared with

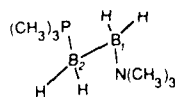


Figure 1. $^{11}B\{^1H\}$ NMR (96.2 MHz) spectrum of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ at +20 °C in CH_2Cl_2 .

the values of $B_2H_4 \cdot 2N(CH_3)_3$ and $B_2H_4 \cdot 2P(CH_3)_3$ in Table I. The $^{31}P\{^1H\}$ NMR spectrum of the compound is a broad, partially collapsed 1:1:1:1 quartet centered at 3.6 ppm with a J_{PB} value of ca. 50 Hz. The apparent absence of a doublet feature ($B-P$ coupling) on the B_P resonance signal (Figure 1) is attributable

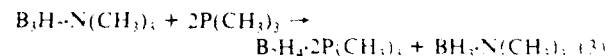
Table I. ^{11}B NMR Shift Data (ppm)

| a. $B_2H_4 \cdot L \cdot L'$ | | | |
|---|-------|-------|--------|
| | B-N | B-P | |
| $B_2H_4 \cdot 2P(CH_3)_3^a$ | | -37.5 | |
| $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ | -2.7 | -36.4 | |
| $B_2H_4 \cdot 2N(CH_3)_3^b$ | -3.5 | | |
| b. $B_3H_8 \cdot L \cdot L' +$ | | | |
| | B-N | B-P | BH_3 |
| $B_3H_8 \cdot 2P(CH_3)_3^{+c}$ | | -39.0 | -10.5 |
| $B_3H_8 \cdot N(CH_3)_3 \cdot P(CH_3)_3^{+c}$ | -12.4 | -41.3 | -10.2 |
| $B_3H_8 \cdot 2N(CH_3)_3^{+b}$ | -15.8 | | -9.7 |

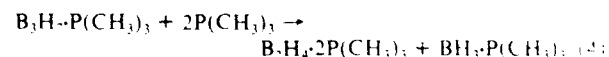
^aReferences 14 and 15. ^bReference 1. ^cReference 3.

to this small J_{BP} value and to the broadness of the signal. The $^1H\{^{11}B\}$ NMR spectrum shows a singlet at 2.52 ppm (intensity 9, amine CH_3 protons), a quintetlike signal at 1.75 ppm (intensity 2, protons on B_N), a sharp doublet at 1.14 ppm ($^2J = 9.0$ Hz, intensity 9, phosphine CH_3 protons), and a doublet of triplets at 0.03 ppm ($^2J_{HBP} = 21$ Hz, $^3J_{HBPH} = 5.0$ Hz, intensity 2, protons on B_P). The quintetlike signal of the protons attached to B_N is thought to be due to spin-spin couplings to both the B_P protons and the phosphorus. On the basis of this assumption, a value of 9.7 Hz is estimated for $^3J_{HBP}$.

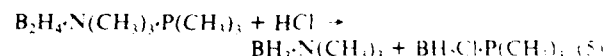
(b) Reactions of $B_3H_8 \cdot N(CH_3)_3$ and $B_3H_8 \cdot P(CH_3)_3$ with $P(CH_3)_3$. The trimethylamine adduct of B_3H_8 slowly reacts with $P(CH_3)_3$ at room temperature in dichloromethane. The major products are $BH_3 \cdot N(CH_3)_3$ and $B_2H_4 \cdot 2P(CH_3)_3$, and $BH_3 \cdot P(CH_3)_3$ and $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ are detected in minute quantities. Thus, the appropriate equation for the reaction is



The reaction of $B_3H_8 \cdot P(CH_3)_3$ with $P(CH_3)_3$ proceeds similarly:

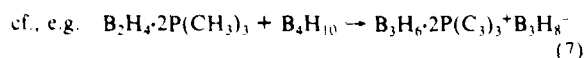
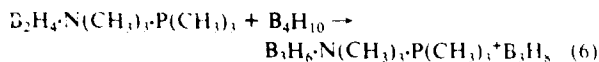


B. Reactions of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$. (a) **With Hydrogen Chloride.** The mixed-base adduct, $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$, reacts with anhydrous HCl at -80 °C in a CH_2Cl_2 solution according to eq 5. Apparently, an alternative mode of cleavage is unfavorable:



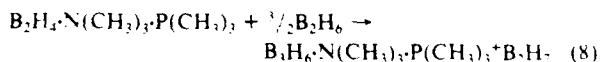
avorable; $BH_3 \cdot P(CH_3)_3$ and $BH_2Cl \cdot N(CH_3)_3$ are produced in trace quantities.

(b) With Tetraborane(10). Treatment of $B_2H_4 \cdot N(CH_3)_3 \cdot P(CH_3)_3$ with B_4H_{10} results in the formation of a new triboron complex cation, (trimethylamine)(trimethylphosphine)hexahydrotriboron(1+) [$B_3H_6 \cdot N(CH_3)_3 \cdot P(CH_3)_3^{+}$] (see eq 6). This reaction is analogous to that of $B_2H_4 \cdot 2P(CH_3)_3$ (eq 7) or $B_2H_4 \cdot 2N(CH_3)_3$ with B_4H_{10} .^{1,3}

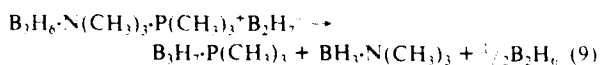


NMR Spectra of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$. Figure 2 shows a $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the salt, $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$. The signal at -30 ppm is readily assignable to the B_3H_8^- anion.⁴ Shown also in Figure 2 is the proposed structure of the $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$ cation, which is similar to those of the $\text{B}_3\text{H}_6\cdot 2\text{N}(\text{CH}_3)_3^+$ ¹ and $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$ ^{3,5} cations. A comparison of the NMR data of these three cations permits an unambiguous assignment of the spectrum (see Table Ib). Thus, the signals at -10.2 , -12.4 , and -41.3 ppm ($J_{\text{BP}} = 116$ Hz) are assigned to the B(3), B(1), and B(2) atoms, respectively, of the new triborane cation. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ shows a well-defined 1:1:1:1 quartet centered at -3.3 ppm with a $^{11}\text{B}-^{31}\text{P}$ spin-coupling constant of 119 Hz. The variable-temperature $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ reveals that the cation is fluxional with respect to migration of the borane hydrogen atoms around the three-boron framework of the cation. At -10°C the borane proton signal appears as a singlet at 1.40 ppm. At -80°C , however, this signal disappears and a singlet signal appears at 2.17 ppm. Other signals of borane protons, which are expected to appear at higher field, could not be identified unequivocally, probably due to the overlap with the phosphine methyl proton signal at 1.39 ppm ($J_{\text{HP}} = 12$ Hz) and the B_3H_8^- proton signal at 0.02 ppm. Shoulders were discernible on both sides of the 0.02 ppm signal. The signal of the amine methyl protons appears at 2.66 ppm.

(c) With Diborane(6). As is the case in the reactions of diborane(6) with $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$,^{1,3} the treatment of $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3$ with B_2H_6 at -65°C produces a B_2H_7^- salt of the $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$ cation:



The product undergoes a slow decomposition at -45°C according to eq 9. The decomposition is fast above 0°C and is quantitative.



An alternative mode of decomposition that would produce $\text{B}_3\text{H}_7\cdot\text{N}(\text{CH}_3)_3$ and $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ does not occur.

Discussion

When the B-B bond of $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ is cleaved as a result of the reaction with an electrophilic reagent (eq 5 or eq 8 and 9), $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ is produced, and the stronger base, $\text{P}(\text{CH}_3)_3$, is attached to the stronger acids, BH_2Cl or B_3H_7^- . Other than this unique feature of the mixed-ligand adduct, the reactions of $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ with electrophilic reagents parallel those of $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$ ¹ and $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$.³ Reaction chemistry of the new mixed-ligand triborane complex cation, $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$, will be described in a separate paper.⁶

Ritter and co-workers⁷ and Parry and Paine⁸ proposed a mechanism for the triborane cleavage reactions. The most important facet of this mechanism is the formation of an intermediate, $\text{B}_3\text{H}_7\cdot\text{L}_0\cdot\text{L}_a$ where L_0 and L_a represent the Lewis base in the reacting B_3H_7 adduct and the attacking Lewis base, respectively. As illustrated in Scheme I, this mechanism adequately

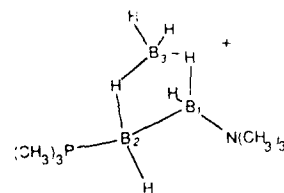
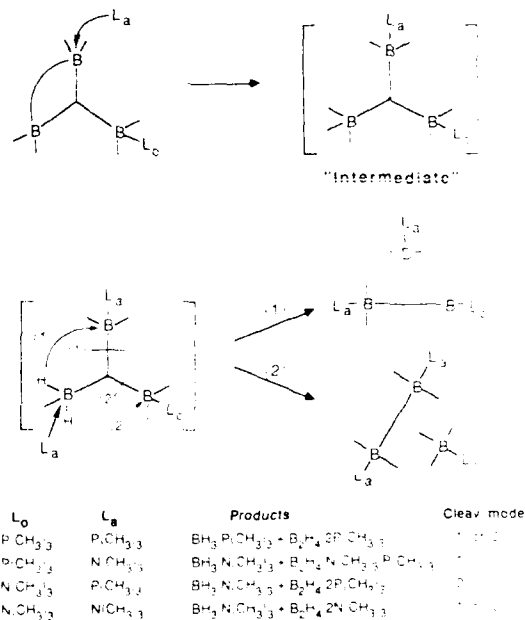


Figure 2. $^{11}\text{B}\{^1\text{H}\}$ NMR (96.2 MHz) spectrum of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ at -20°C in CD_2Cl_2 .

Scheme I



explains the observed formation of the B_2H_4 adducts containing $\text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$. It is noted that, whenever amine is involved in the reaction, $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ is produced, indicating that elimination of $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ from the intermediate is favored over $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ elimination.

In the early days, the reaction of a triborane(7) adduct of a strong base [e.g., $\text{B}_3\text{H}_7\cdot\text{N}(\text{CH}_3)_3$] with a strong base [e.g., $\text{N}(\text{CH}_3)_3$] was thought to give a complex mixture of borane compounds containing polymeric species.⁹ The newly observed formation of the B_2H_4 adducts of strongly basic $\text{P}(\text{CH}_3)_3$ and $\text{N}(\text{CH}_3)_3$ corrects this earlier misconception.

Experimental Section

General Procedures. Conventional vacuum-line techniques were used throughout. Transfer of air-sensitive solids was performed in a plastic glovebag filled with dry nitrogen gas. The sources of B_2H_6 , B_4H_{10} , $\text{P}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_3$, and dichloromethane were described previously. Some samples of B_2H_6 were prepared from $(\text{CH}_3)_4\text{N}^+\text{B}_2\text{H}_6^-$ by the treatment with $\text{BF}_3\cdot\text{OEt}_2$. The NMR spectra were obtained on a Varian XL-300 spectrometer, the observe frequencies being 96.2, 121.4, and 299.9 MHz for ^{11}B , ^{31}P , and ^1H , respectively. Chemical shifts are expressed in ppm. Standards for the shifts are $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ and 85%

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THE CONVERSION OF SMALLER BORANE FRAGMENTS TO LARGER

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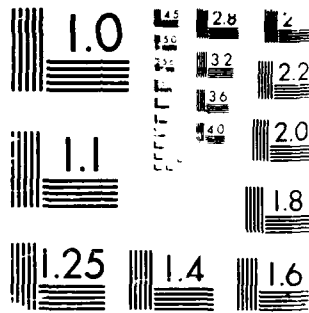
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H_3PO_4 for boron and phosphorus, respectively. Proton shifts are given with respect to the resonance signal of proton impurity in CD_2Cl_2 , which was taken as 5.28 ppm. Shifts to lower fields are assigned positive values. Generally, reactions were run in 9–10 mm o.d. Pyrex tubes or in 10 mm o.d. resealable NMR sample tubes (products of J. Young, Ltd.) and were monitored on the NMR instrument by observing ^{11}B spectra.

Reaction of $\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3$ with $\text{N}(\text{CH}_3)_3$. A 1.0-mmol sample of $\text{N}(\text{CH}_3)_3$ was condensed into a reaction tube containing 0.50 mmol of $\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3$ (prepared from B_2H_{10} and $\text{P}(\text{CH}_3)_3$ ¹²) and approximately 1 mL of CH_2Cl_2 . The reactants were mixed well at -80°C and then allowed to warm slowly. When the temperature reached about 20°C , the reactants had been completely converted to a mixture of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ and $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ (-8.3 ppm).¹³ The solvent and the BH_3 adduct were pumped out at -45 and 0°C , respectively, and the remaining solid residue was sublimed under high vacuum at room temperature onto a 0°C cold finger.

Samples of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ for reaction studies were prepared by allowing the initial mixture of reactants to stand at room temperature for 15 min and then by removing the solvent and the $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ as described above. The solid residues thus obtained were sufficiently pure for general use.

Reaction of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3$ with $\text{P}(\text{CH}_3)_3$. A 1.05-mmol sample of $\text{P}(\text{CH}_3)_3$ was condensed onto a frozen CH_2Cl_2 solution containing 0.49 mmol of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3$, and the solution was mixed thoroughly at -80°C . Trimethylamine-borane(3) and $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ (-37.5 ppm)^{14,15} slowly formed in the reaction mixture at room temperature. The reaction was nearly complete after 3 h at this temperature.

Reaction of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ with HCl. Anhydrous HCl (0.25 mmol) was condensed into a reaction tube containing 0.18 mmol of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ and approximately 1 mL of CH_2Cl_2 frozen at -196°C . As the mixture was allowed to melt, the reaction occurred immediately. The ^{11}B NMR spectrum of the reaction mixture indicated the formation of $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ and $\text{BH}_2\text{Cl}\cdot\text{P}(\text{CH}_3)_3$ (-18.8 ppm)⁴ with traces of $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ (-37.1 ppm)⁴ and $\text{BH}_2\text{Cl}\cdot\text{N}(\text{CH}_3)_3$ (-7.8 ppm).¹³

Reaction of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ with B_3H_6 . A 0.55-mmol sample of B_2H_{10} was condensed into a 10-mm NMR tube containing 0.50 mmol of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ and approximately 1 mL of CH_2Cl_2 . The reactants were mixed well at -80°C and then allowed to slowly warm. At -60°C the formation of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{B}_3\text{H}_6$ was observed. Then, the tube was warmed to room temperatures to ensure that

the reaction had gone to completion. The solution was then cooled to -10°C , and the solvent and unchanged B_2H_{10} were removed by pumping. The resulting white solid residue, $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{B}_3\text{H}_6$, was redissolved in CD_2Cl_2 for the NMR study.

Reaction of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ with B_3H_6 . A 0.81-mmol sample of B_3H_6 was condensed into a reaction tube containing 0.52 mmol of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ and approximately 1 mL of CH_2Cl_2 . The reactants were mixed well at -80°C , and then the tube was allowed to warm slowly. At -65°C the formation of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{B}_3\text{H}_6$ was observed. At -45°C the reaction was faster, and the formation of $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3$ (-15.6 and -45.0 ppm)¹⁶ was observed. When the temperature reached 25°C , only the signals of $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$, $\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3$, and B_3H_6 were present.

Acknowledgment. We gratefully acknowledge the support of this work by the U.S. Army Research Office through Grant DAAG 29-85-K-0034. Financial support to R.F.D. from the National Science Foundation (Minority Graduate Fellowship, 1981–1984) is appreciated. The NMR instrument was acquired with the use of instrumentation funds that were provided by the National Science Foundation and the Department of Defense.

Registry No. $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$, 97551-46-7; $\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3$, 97012-38-9; $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3$, 57808-48-7; $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$, 75-22-9; $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$, 67113-98-8; $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$, 1898-72-7; $\text{BH}_2\text{Cl}\cdot\text{P}(\text{CH}_3)_3$, 64160-46-9; HCl, 7647-01-0; B_2H_{10} , 18283-93-7; $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{B}_3\text{H}_6$, 112925-44-7; B_3H_6 , 19287-45-7; $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{B}_3\text{H}_6$, 112968-02-2.

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Formation of Diboron Complex Cations

Rosemarie E. DePoy and Goji Kodama*

Received October 16, 1987

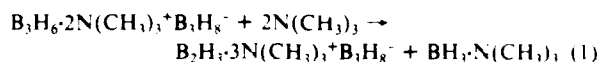
Earlier, we reported briefly that the reaction of bis(trimethylamine)hexahydrotriboron(1+) octahydrotriborate(1-), $B_3H_6 \cdot 2N(CH_3)_3^+ B_3H_8^-$, with trimethylamine resulted in the cleavage of the triboron cation framework to produce a new

Table I. Chemical Shift Values for the Diboron Complex Cations^a

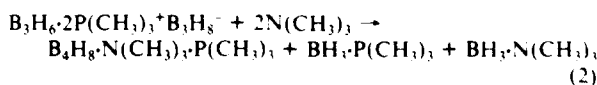
| | | $\begin{array}{c} \text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}-\text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}_2-\text{P(CH}_3)_3 \\ \\ \text{H} \end{array}$ | $\begin{array}{c} \text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}-\text{P(CH}_3)_3 \\ \\ \text{H}-\text{B}_2-\text{P(CH}_3)_3 \\ \\ \text{H} \end{array}$ | $\begin{array}{c} \text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}-\text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}_2-\text{N(CH}_3)_3 \\ \\ \text{H} \end{array}$ | $\begin{array}{c} \text{N(CH}_3)_3 \\ \\ \text{H}-\text{B}-\text{P(CH}_3)_3 \\ \\ \text{H}-\text{B}_2-\text{N(CH}_3)_3 \\ \\ \text{H} \end{array}$ |
|-----------------|----------------------|--|--|--|--|
| | | I | II | III | IV |
| ¹¹ B | B(1) | +11.4 | -5.8 | +12.5 | -5.4 |
| | B(2) | -34.7 | -35.8 | -3.9 | -5.4 |
| ³¹ P | P(1) | | -14.2 | | 13.0 |
| | P(2) | +1.9 | +0.5 | | |
| ¹ H | H _{NMe} (1) | 2.68 | 2.67 | 2.75 | 2.72 |
| | H _{NMe} (2) | | | 2.51 | 2.54 |
| | H _{PMc} (1) | | 1.39 ^b | | 1.44 ^b |
| | H _{PMc} (2) | 1.20 ^b | 1.22 ^b | | |

^a The shift values are expressed in ppm. Standards for the shifts: ¹¹B, BF₃·O(C₂H₅)₂; ³¹P, 85% orthophosphoric acid; ¹H, CH₂Cl₂ signal at 5.28 ppm. Low-field shifts are taken as positive. ^b Doublet, *J*_{HP} = 10 Hz. ^c Doublet, *J*_{HP} = 11 Hz.

diboron complex cation, tris(trimethylamine)trihydrodiboron(1+), as indicated in eq 1.¹ This reaction contrasted sharply with our



earlier observation² on the reaction of B₃H₆·2P(CH₃)₃·B₃H₈⁻ with N(CH₃)₃, which produced the tetraborane(8) adduct according to eq 2. The reaction of B₃H₆·2P(CH₃)₃·B₃H₈⁻ with P(CH₃)₃

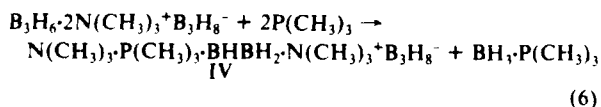
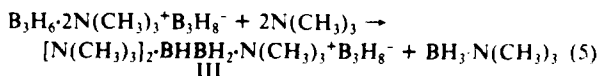
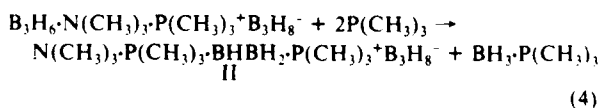
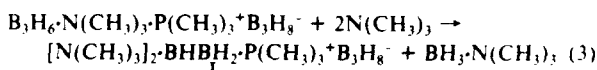


proceeded similarly to give B₄H₈·2P(CH₃)₃.²

As a result of the recent, successful isolation of B₂H₄·N(C₂H₅)₃·P(CH₃)₃ in pure form, another triboron complex cation, B₃H₆·N(CH₃)₃·P(CH₃)₃, became available.³ It was of interest to see how the B₃H₈⁻ salt of this "hybrid" cation would respond to the treatment with N(CH₃)₃ or P(CH₃)₃. In this paper, results of the reaction studies of B₃H₆·N(CH₃)₃·P(CH₃)₃·B₃H₈⁻ are described and are compared with corresponding reactions of B₃H₆·2N(CH₃)₃·B₃H₈⁻ and B₃H₆·2P(CH₃)₃·B₃H₈⁻.

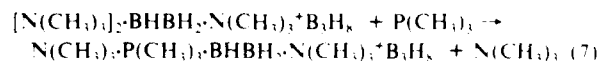
Results

Reactions of B₃H₆·N(CH₃)₃·P(CH₃)₃·B₃H₈⁻ and B₃H₆·2N(CH₃)₃·B₃H₈⁻ with N(CH₃)₃ or P(CH₃)₃ proceeded according to eq 3–6.



Generally, these reactions are clean and virtually quantitative as long as the reaction solutions are kept below the decomposition temperatures of the respective products. As the reaction proceeded, the signals of the N(CH₃)₃ or P(CH₃)₃ adduct of BH₃ and the diboron complex cation grew in the ¹¹B NMR spectrum of each reaction solution while the signals of the triboron complex

cation diminished and that of B₃H₈⁻ remained unchanged. Compound IV is the most stable of the four diboron cations, and most of the coproduct, BH₃·P(CH₃)₃, can be sublimed out at 0 °C. Above 0 °C, however, this salt decomposes slowly. This compound can also be prepared from III by a ligand displacement reaction (eq 7). Salt III is the least stable and undergoes de-



composition at -40 °C. Compounds I and II decompose slowly at -30 °C. Because of their limited stabilities, the salts were characterized by their NMR spectra as they were formed, in the presence of the coproducts BH₃·N(CH₃)₃ or BH₃·P(CH₃)₃.

NMR Spectra and Structures of the Diboron Complex Cations.

The chemical shift data for the four diboron cations, I–IV, are listed in Table I.

(a) **1,1-Bis(trimethylamine)-2-(trimethylphosphine)trihydrodiboron(1+) Cation**, [N(CH₃)₃]₂·BHBH₂·P(CH₃)₃⁺ (I). The two broad signals at +11.4 and -34.7 ppm in the ¹¹B{¹H} NMR spectrum could readily be assigned to the two-amine-attached boron and the phosphine-attached boron atoms, respectively. Furthermore, the presence of only one amine methyl proton signal and its intensity 2 relative to that of the phosphine methyl proton signal supported the designated structure of this cation.

(b) **1-(Trimethylamine)-1,2-bis(trimethylphosphine)trihydrodiboron(1+) Cation**, N(CH₃)₃·P(CH₃)₃·BHBH₂·P(CH₃)₃⁺ (II). The broad signal at -5.8 ppm in the ¹¹B{¹H} spectrum was attributed to the boron atom attached to both an amine group and a phosphine group, and the signal at -35.8 ppm could be attributed to the phosphine-attached boron atom. The presence of two phosphine methyl proton signals was also consistent with the structure assigned to this cation.

(c) **1,1,2-Tris(trimethylamine)trihydrodiboron(1+) Cation**, [N(CH₃)₃]₃·BHBH₂·N(CH₃)₃⁺ (III). As reported earlier¹ the ¹¹B resonance signals appeared at +12.5 and -3.9 ppm, which were assigned to the two-amine-attached boron and one-amine-attached boron atom, respectively. The presence of the two amine methyl proton signals in a 2:1 intensity ratio is consistent with the designated structure of this cation.

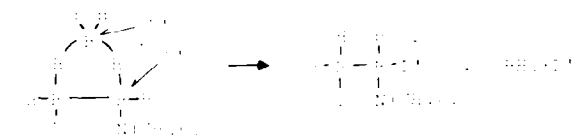
(d) **1,2-Bis(trimethylamine)-1-(trimethylphosphine)trihydrodiboron(1+) Cation**, N(CH₃)₃·P(CH₃)₃·BHBH₂·N(CH₃)₃⁺ (IV). The ¹¹B{¹H} spectrum showed only one broad signal at -5.4 ppm, which is due to the overlapping of signals arising from the two nonequivalent boron atoms in the cation. This assignment is made on the basis of the relative intensities of the signals present in the spectrum of the reaction solution: the signal at -5.4 ppm; intensity 2, B₃H₈⁻ signal; intensity 3, and BH₃·P(CH₃)₃ signal; intensity 1. These two coincidental signals at -5.4 ppm could not be resolved even on a Varian XL-400 instrument (¹¹B observation frequency, 128 MHz). However, on this high-field instrument the application of resolution enhancement techniques did indicate a dissymmetry attributable to the overlapping of these two signals. Furthermore, the presence of two trimethylamine proton signals in a 1:1 intensity ratio verified the identity of this cation.

(1) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2871.

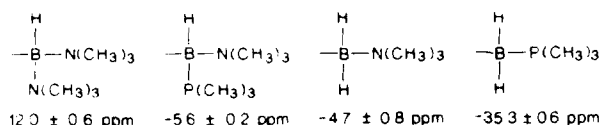
(2) Kameda, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3710.

(3) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 1116.

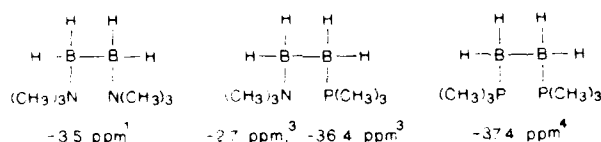
Scheme I



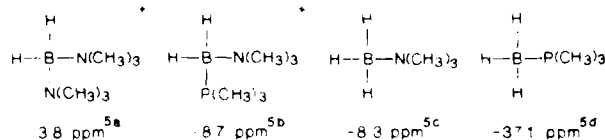
Summary of ^{11}B Shift Values. The following ^{11}B group shift values are found for the diboron complex cations:



When trimethylamine is replaced by trimethylphosphine on the adjacent boron atom, the ^{11}B resonance moves upfield only slightly. For example, in going from $[\text{N}(\text{CH}_3)_3]_2\text{B}_2\text{H}_6^+$ to $[\text{N}(\text{CH}_3)_3]_2\text{B}_2\text{H}_6^+$, the ^{11}B shift value of the $[\text{N}(\text{CH}_3)_3]_2\text{BH}$ group decreases by 1.1 ppm. Thus, each of the ^{11}B shift values for these groups is essentially constant regardless of the type of ligands ($\text{N}(\text{CH}_3)_3$ or $\text{P}(\text{CH}_3)_3$) attached to the adjacent boron atom. Furthermore, the values listed above are comparable with those for $\text{B}_2\text{H}_4\cdot\text{L}\cdot\text{L}'$:

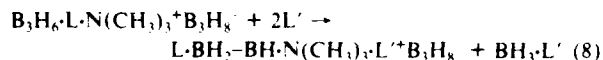


The values further compare with those reported for the following monoborane species:



Discussion

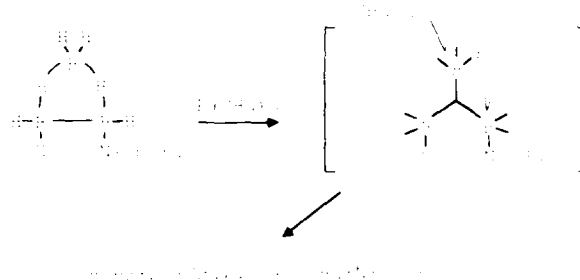
There are two important features that are common to the reactions represented by eq 3-6: (1) In the diboron complex cations produced, the attacking Lewis base is always bonded to the amine-attached boron atom, and (2) the BH_3 adduct that is formed always contains the attacking Lewis base. Thus, the four reactions can be summarized by eq 8, where L and L' are $\text{N}(\text{CH}_3)_3$



or $\text{P}(\text{CH}_3)_3$ and L' is the attacking base. Apparently, the bond cleavages occur as indicated in Scheme I. This observation immediately provides a "partial" explanation for the behavior of $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ toward $\text{P}(\text{CH}_3)_3$ or $\text{N}(\text{CH}_3)_3$ (eq 2). Because of the absence of a trimethylamine-attached boron atom in the $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$ cation, the attacking base, L', cannot find an effective site of attack on the $(\text{CH}_3)_3\text{P-B-B-P}(\text{CH}_3)_3$ moiety to produce a $\text{B}_2\text{H}_5\cdot 2\text{P}(\text{CH}_3)_3\cdot\text{L}'^+$ cation.

The Lewis base adducts of triborane(7) are isoelectronic and isostructural with the triboron complex cations. Interestingly, however, the above pattern of triboron cation cleavage contrasts with those observed for the cleavage of $\text{B}_3\text{H}_8\cdot\text{N}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_7\cdot\text{P}(\text{CH}_3)_3$ with $\text{N}(\text{CH}_3)_3$ or $\text{P}(\text{CH}_3)_3$, where the BH_3 adducts produced contain $\text{N}(\text{CH}_3)_3$ whenever $\text{N}(\text{CH}_3)_3$ is involved in the reaction system.³ For example, $\text{B}_3\text{H}_7\cdot\text{N}(\text{CH}_3)_3 + 2\text{P}(\text{CH}_3)_3 \rightarrow$

Scheme II



$\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3 + \text{BH}_3\cdot\text{N}(\text{CH}_3)_3$. This observation was explained³ by extending the mechanism proposed by Ritter and co-workers⁶ and by Paine and Parry,⁷ as a result of favorable elimination of $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ from the reaction intermediate $[\text{B}_3\text{H}_6\cdot\text{P}(\text{CH}_3)_3\cdot\text{N}(\text{CH}_3)_3]^+$. Upon further $\text{P}(\text{CH}_3)_3$ attack on the intermediate, $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ splits off from the intermediate and the attacking base $\text{P}(\text{CH}_3)_3$ is combined with the B_3H_6 fragment as illustrated in Scheme II. This mechanistic model for the triborane(7) adduct cleavage does not explain the observed cleavage pattern of the triboron cations. Reactivity variation due to the presence of charge and the nature of ligand is demonstrated in these triboron framework cleavages. Further studies are being pursued to elucidate the triboron framework cleavage processes, in which Lewis bases play subtle, but important roles.

Experimental Section

General Procedures for the Reaction Studies. A dichloromethane solution (ca. 2 mL) of the triboron complex cation was prepared in a 10 mm o.d. Pyrex tube or a 10 mm o.d. resealable NMR sample tube (product of Young Ltd.). A measured amount of $\text{N}(\text{CH}_3)_3$ or $\text{P}(\text{CH}_3)_3$ was condensed onto the solution at liquid-nitrogen temperature. The solution was mixed well at -80°C , and then the tube was placed in the precooled probe of a Varian XL-300 NMR spectrometer to monitor the reaction as the temperature of the probe was raised stepwise.

Reagents. The B_3H_8^+ salts of the triboron complex cations were prepared in the reaction tubes according to the reported methods.¹⁻³ The salt was isolated as a solid in the tube, and then a fresh portion of the solvent was condensed into the tube to prepare the solution. The trimethylamine, trimethylphosphine, and dichloromethane used were from our laboratory stock.⁸

Reactions. (a) $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ and $\text{N}(\text{CH}_3)_3$. A 0.65-mmol sample of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ was treated with 1.45 mmol of $\text{N}(\text{CH}_3)_3$. The signals of the products (the diboron cation (I) and $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$) were detected at -80°C . The reaction was complete as the probe temperature was raised to -60°C . At -20°C , signals due to decomposition products began to appear slowly in the spectrum.

(b) $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ and $\text{P}(\text{CH}_3)_3$. A 0.49-mmol sample of $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ was treated with 0.98 mmol of $\text{P}(\text{CH}_3)_3$. When the reaction mixture was allowed to warm to -30°C , the reactants had been changed to a 1:1 molar mixture of $\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3\cdot\text{BHBH}_2\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ (II) and $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$. At this temperature, slow decomposition of the salt occurred as evidenced by the appearance of the $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ signal in the spectrum of the solution.

(c) $\text{B}_3\text{H}_6\cdot 2\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ and $\text{N}(\text{CH}_3)_3$. A sample (normally about 0.5 mmol) of $\text{B}_3\text{H}_6\cdot 2\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ was treated with 2 molar equiv or more of $\text{N}(\text{CH}_3)_3$. Conversion of the reactants to $[\text{N}(\text{CH}_3)_3]_2\cdot\text{BHBH}_2\cdot\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^+$ (III) and $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$ was complete at -60°C . Above -40°C (or even at -50°C , upon irradiation of the solution with the ^1H resonance frequencies for decoupling the ^1H spins), decomposition of the diboron cation occurred. The decomposition product(s) had its characteristic ^{11}B signals at -2.9 and 13.3 ppm, and the B_3H_8 signal was present. The nature of the decomposition product has not been elucidated.

Conversion of III to IV. A sample containing III, which had been prepared as above, was mixed with 1 molar equiv of $\text{P}(\text{CH}_3)_3$ at -80°C in CH_2Cl_2 . At -45°C changes in the spectrum were noted. After the mixture was stored for 2.5 h at -30°C , III had been converted completely to IV. Treatment of III with a 3-fold excess of $\text{P}(\text{CH}_3)_3$ at -30°C

(4) Hertz, R. K.; Denniston, M. L.; Shore, S. G. *Inorg. Chem.* **1978**, *17*, 2673.

(5) Nöth, H.; Wrackmeyer, B. In *NMR, Basic Principles and Progress*; Diehl, P.; Fluck, E.; Kosfeld, R., Eds.; Springer-Verlag: West Berlin, Heidelberg, FRG, 1978; Vol. 14. (a) p 377; (b) p 380; (c) p 285; (d) p 341.

(6) Deever, W. R.; Lory, E. R.; Ritter, D. M. *Inorg. Chem.* **1969**, *8*, 1263.

(7) Paine, R. T.; Parry, R. W. *Inorg. Chem.* **1975**, *14*, 689.

(8) Kameda, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3710.

$^{\circ}\text{C}$ and at 0°C did not bring about a further displacement of $\text{N}(\text{CH}_3)_3$ from IV.⁹

(d) $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ and $\text{P}(\text{CH}_3)_3$. A sample of $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ was treated with $\text{P}(\text{CH}_3)_3$ in a manner similar to that used for preparation c. Formation of $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ was noted at -30°C . The reaction was slow at -20°C . Although the reaction proceeded with a moderate rate to completion at $+10^{\circ}\text{C}$, weak signals of decomposition products were noted in the ^{11}B spectrum of the final solution.

Acknowledgment. This work was supported by the U.S. Army Research Office through Grant DAAG 29-85-K-0034. The NMR instrument was acquired with the use of instrumentation funds that were provided by the National Science Foundation and the Department of Defense. Financial support to R.E.D. from the National Science Foundation (Minority Graduate Fellowship, 1981-1984) is appreciated.

Registry No. I, 113810-98-3; II, 113811-00-0; III, 113811-03-3; IV, 113811-02-2; $\text{B}_3\text{H}_6 \cdot \text{N}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$, 112925-44-7; $\text{B}_3\text{H}_6 \cdot 2\text{N}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$, 113810-96-1; $\text{N}(\text{CH}_3)_3$, 75-50-3; $\text{P}(\text{CH}_3)_3$, 594-09-2; $\text{BH}_3 \cdot \text{N}(\text{CH}_3)_3$, 75-22-9; $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$, 1898-77-7.

(9) This observation was made by M. Kameda of this laboratory.

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